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CHEMICAL RESEARCH, -DEVELOPMENT & ENGINEERING CENTER

CRDEC-TR-053

A STUDY
OF CANDIDATE REPLACEMENT MATERIALS
FOR DOP IN FILTER-TESTING
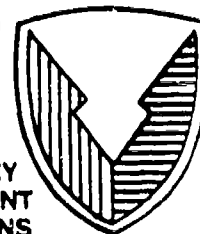# PENETROMETER MACHINES

Hugh R. Carlon
U.S. Army Fellow

Mark A. Guelta

RESEARCH DIRECTORATE

Bernard V. Gerber

OPTIMETRICS, INC.
Ann Arbor, MI 48105-9748

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Aberdeen Proving Ground, Maryland 21010-5423

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For many decades dioctyl phthalate (DOP) has been the standard material used by the
U.S. Army and many other agencies to simulate aerosol behavior in the performance of
non-destructive gas mask and filter serviceability testing and vehicle or shelter
penetration/vulnerability tests. Now, The U.S. Army Surgeon General has taken the
position that DOP is a suspected carcinogen. Testing with DOP has been placed under
tight controls, or stopped altogether. A safe replacement material for DOP is needed
urgently.

In this study, several classes of candidate DOP replacement materials having low
inherent toxicities were identified by searches of computer data bases and Material
Safety Data Sheets (MSDS) and discussions with manufacturers of materials recently
introduced to the marketplace. About three dozen samples of promising materials were
obtained and tested in two, filter-penetrometer machines: (1) a standard Q127 machine
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LAMAPP	Quality assurance	Synthetic hydrocarbons
Isostearic acid	Nucleation	Fatty acid esters. (A U),
Oleic acid	Smokes (test),	Carcinogenicity
Vendors	Manufacturers	Laser aerosol spectrometer

19. Abstract (continued)

of the type used worldwide in gas mask filter testing, utilizing a "hot smoke" generating scheme, and (2) the Los Alamos Monodispersed Aerosol Prototype Penetrometer (LAMAPP), a state-of-the-art developmental "cold smoke" generating system. Both machines had previously been shown to work well with DOP, producing test smokes meeting the accepted standard: geometric mean diameter (GMD) = 0.3 μm, and geometric standard deviation (GSD) less than 1.3, with suitable aerosol mass concentration for filter testing.
Several materials were identified that are viable candidates to replace DOP in both machines, and in filter testing generally, including isostearic acid, certain synthetic hydrocarbons, and oleic acid. These are ranked, for each machine, in order of probable success and recommended for use subject to toxicological screening and anticipated approval. The U.S. Army Armament, Munitions and Chemical Command (AMCCOM), Product Assurance Directorate (PAD), and Los Alamos National Laboratory (LANL) were notified of these results in October 1988, with the recommendation that acceptance testing be initiated immediately (on a large scale, in the case of the Q127 and other "hot" machines).
The recommended replacement materials are inexpensive and readily available, and should prove to be at least as stable in long-term operation as DOP. Over the longer term, it is recommended that improvements to Q127 and other "hot" machines in the field be considered as outlined here, and that, concurrently, the development of a new-generation penetrometer based on LAMAPP be pursued. Finally, it is recommended that these materials be evaluated to replace substances such as corn oil in a variety of testing applications in which spray-generated aerosols having broad particle size distributions are presently used.

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PREFACE

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A STUDY OF CANDIDATE REPLACEMENT MATERIALS FOR DOP

IN FILTER-TESTING PENETROMETER MACHINES.

1. INTRODUCTION.

1.1 Background.

The properties and environmental hazards of DOP (dioctyl phthalate) are given in Appendix A from Reference 1. DOP is known by many synonyms, including:

- di (2-ethylhexyl) phthalate;

- bis (2-ethylhexyl) phthalate;

- di-sec-octyl phthalate;

- phthalic acid;

- bis (2-ethyihexyl) ester;

- di (2-ethylhexyl) orthophthalate;

- 1,2 benze edicarboxylic acid (bis (2-ethylhexyl) ester).

The chemical formula of DOP is

$$C_6H_4(COOCH_2CH(C_2H_5)(CH_2)_3CH_3)_2.$$
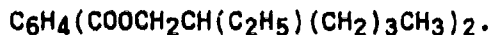
For many decades DOP, a common industrial plasticizer with many uses, has been used by the U.S. Army and other agencies to simulate aerosol behavior in the performance of non-destructive gas mask and filter servicability testing and vehicle or shelter penetration/vulnerability tests. Filter testing with DOP has become completely standardized, and hundreds of penetrometer machines have been fabricated from standard plans and have been put into service at dozens of locations worldwide.

During 1985 and 1986, concern continued to grow that DOP was a potential carcinogen. The U.S. Army Surgeon General decided to take the position that DOP is to be considered a suspect carcinogen, and in April of 1986 instructions were issued to Army commands stating that testing with DOP would be placed under tight controls (Appendix B).

Workers occupationally exposed to DOP aerosols and liquid were ordered to be taken under medical surveillance, to be issued approved personal protective equipment if warranted, to be subject to engineering controls to reduce their exposures, and to have industrial hygiene assessments provided of their exposures.

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Workers were to be formally advised of the risks associated with working with DOP. Work areas were to be labeled as "Cancer Suspect Agent Areas", and access was to be limited only to authorized personnel. U.S. Army Armament, Munitions and Chemical Command (AMCCOM) organizations were were required to provide that headquarters with seven different kinds of compliance information.

These actions placed severe restrictions upon routine, 100% quality assurance testing and assessment of filters and other equipment. Accordingly, Engineering Study Proposal (ESP) FI-7-8860, "Alternative for DOP", was issued by Product Assurance Directorate (PAD), AMCCOM, containing the following statement of the problem:

"Due to the potential health hazard in using DOP for aerosol testing, it is recommended that an Engineering Study be undertaken to iden- tify alternative material(s) from which can be generated stable and safe (does not present potential health problem) monodispersed aerosol. In addition, test parameters for all affected test specifications shall be revised to insure proper quality insurance when testing with the new material(s)."

The objective and proposed solution of the study program was "to remove the chemical dioctyl phthalate (DOP) from penetration test equipment and specifications and provide a relatively innocuous substitute with mini- mal impact to existing hardware".

The problem was assigned to scientists of the Physics Division (PD), Research Directorate (RD), U.S. Army Chemical Research, Development and Engineering Center (CRDEC), for program planning and execution beginning in FY1988 and ending several months into FY1989. Following meetings between PD and Product Assurance Directorate (PAD) representatives, a test plan was developed and approved (Appendix C).

1.2   The Test Plan.

The test plan includes a statement of work to be performed by Research Directorate (RD) scientists. It provides for the availability of penetrometer machines, the selection of candidate replacement materials for DOP based upon their toxicology, physical properties, cost, and other factors, and the screening of these materials leading to the recommendation that one (or more) of them be evaluated at PAD using testing machines including the Q127, the Q107, and the Q76 (or the equivalent Q233).

1.2.1   The Penetrometer Machines.

The Test Plan provides that assessments of candidate replacement materials for DOP could be carried out concurrently using two different kinds of respirator canister HEPA filter testing or penetrometer machines:

● The Q127 penetrometer machine (Appendix D);

● The "LAMAPP" prototype penetrometer machine (Appendix E).

LAMAPP is an acronym for "Los Alamos Monodispersed Aerosol Prototype Penetrometer". This cart-mounted, prototype system was designed and built for PAD under contract with the Los Alamos National Laboratory. It incorporates state-of-the-art technology including cold-aerosol generation (a heated reservoir or "pot" is not used).

The LAMAPP system incorporates a "LAS-X" Laser Aerosol Spectrometer (Appendix E), which measures particle count mean diameter (CMD) of sampled aerosols in four ranges between 0.09μm and 3.00μm. Fifteen channels of size resolution are provided in each channel. The LAS-X is connected to a small computer which is programmed to compute the geometric standard deviation (GSD) of a given sample aerosol and to print out a graphical representation of the aerosol size distribution with a table of data which includes the CMD and GSD.

Many examples of printouts from the LAS-X/computer system are included in Appendix I of this report. The Engineering Study Proposal (ESP) stated that the desired result is a test aerosol or smoke, to replace DOP, having a CMD of 0.3μm, a mass concentration of 100 mg/m^3, and a GSD equal to or less than 1.3. GSD is often referred to as σ_g, pronounced "sigma g".

By using suitable aerosol dilution equipment in the RD studies, it has been possible to employ the LAS-X/computer system not only to monitor CMD and GSD or σ_g of aerosols generated by the LAMAPP, but those generated by a Q127 machine as well. In this way comparable data are obtained from both machines, and the performance of the Q127 can be checked against values of particle size indicated by the "Owl" nephelometer, which has been standard on the Q127 for many decades (Appendix D).

Only brief, introductory information has been given here concerning the penetrometer machines used in this program. These machines are described in greater detail in Appendixes D and E. A detailed discussion of the experimental facility is given in Section 2.0.

1.2.2   Selection of Candidate Materials.

1.2.2.1   Toxicological Properties of DOP and Candidate Materials.

B.V. Gerber, a co-author of the present report, has considered in detail the toxicology data base of the polyethylene glycols in a careful investigation of candidate replacement materials for DOP.[2] His paper, Reference 2, which is reproduced in Appendix F here, contains many references to publications bearing on the toxicity of DOP and of potential replacement materials.

Gerber relates that on October 15, 1980, the National Cancer Institute reported bioassay data on rats and mice indicating that DOP causes increased incidence of hepatocellular carcinomas or neoplastic nodules in rats and hepatocellular carcinomas or adenomas in mice.

The U.S. Occupational Safety and Health Administration (OSHA) subsequently classified DOP as a Category I potential carcinogen, requiring that if there are substitutes available that are less hazardous to humans than DOP there shall be no occupational exposure to DOP. The use of DOP would be precluded wherever the practicability of a replacement could be demonstrated.   11

Toxicological properties of candidate materials thus became of paramount importance in the present study. Classes or families of materials known to be relatively innocuous had to be screened for possible candidates, which at the same time had physical properties such that they could produce acceptable aerosols in testing machines, and ideally had other inducements to their use such as low cost.

Material Safety Data Sheets (MSDS) were compiled for promising materials, which included straight-chain saturated hydrocarbons (cosanes), moderately branched-chain saturated hydrocarbons, fatty acids, fatty acid esters, and glycols. The MSDS indicated that virtually all of these materials were classed as having very low toxicity to humans. Many, in fact, were approved for use in foods and cosmetics. But virtually no data were found to exist concerning the inhalation toxicity to humans of these materials when breathed as fine aerosols or smokes.

It was recognized that military fog oils comprise large fractions of hydrocarbon materials including those of interest as DOP replacement candidates. Extensive studies have been carried out on the inhalation toxicities of fog oil and related aerosols, and a final report has been drafted which was obtained and reviewed.[3] This report indicates that fog oil contains a great many impurities, and that the impurities themselves probably contribute very significantly to the toxicity of fog oil smokes. Thus, nothing relevant to the DOP replacement problem concerning the human toxicity of oil aerosols could be applied to the present study from Reference 3.

White, et al,[4] independently carried out toxicological screening of candidate DOP replacement materials in support of the present program. A brief summary of their methodology and findings is presented in Appendix G. They also carried out and reported[4] candidate screening based on the physical (and chemical) properties of various materials, as discussed in Appendix H. and in the next section of the present report.

Although some classes of materials identified by White, et al, as viable candidates for DOP replacement have been experimentally investigated in the present work, little is known about the toxicological properties of many other materials including some of the most promising ones reported here.

Thus, in the final analysis, the procedure that must be adopted to find the best and safest material(s) to replace DOP in filter penetrometer testing is a two-fold one:

● Find that material or those materials that work best in the Q127 and LAMAPP machines from the standpoints of reproducible particle size, size distribution, smoke concentration, availability, and cost;

● Subject the material(s) to rigorous toxicological screening, while at the same time carrying out replacement testing in production and/or product assurance facilities, using appropriate safety precautions, so that final approval for use of the material(s) to replace DOP will be automatic when toxicological approval is received; should there be problems other than toxicological ones with the replacement material(s), this can only be determined during long-term testing at the facilities indicated.

1.2.2.2 Physical Properties of Candidate Materials.

Many physical properties appear to play some role in the behavior
of candidate materials when they are used in filter penetrometer machines
such as the Q127. Among these physical properties are vapor pressure, sur-
face tension, viscosity, and density.

At the outset of the present program, regularly-scheduled meetings
were held by the authors and their co-workers for the purpose of compiling
physical property data for many potential candidate materials and comparing
these to data for DOP. The potential candidate materials were selected init-
ially from those for which a CRDEC database already existed.

Table 1 shows comparisons with physical properties of DOP for sev-
eral materials which are identified at the bottom of the table. First,
second, and third choices are shown, based on a computer matching and rank-
ing program, for vapor pressure and for combinations of vapor pressure with
other properties. The numbers are an indication of how good the physical
property matches are to DOP. A value of 1.00 would indicate a perfect match.
Tetraethylene glycol is seen to be a promising candidate, based on the
available data and the constraints of the exercise.

Table 2 shows best fits of physical property data from among many
potential candidate materials considered; here, only one property is con-
sidered at a time. Diisooctyl phthalate is seen to give a better match
with DOP than other materials for several physical properties, but its
structural similarity to DOP (dioctyl phthalate) itself suggests that it
also is likely to have unpromising toxicological properties.

Figure 1 presents a Clausius-Clapeyron plot for several potential
candidate materials, relating the logarithm of vapor pressure to the reciprocal
of absolute temperature in degrees Kelvin. The upper scale on the abscissa also
gives temperature in degrees Celsius. The negative slope of the curve for
each material corresponds to its heat of vaporization divided by the gas
constant. Such curves are readily constructed if vapor pressures for a given
material are known at two or more temperatures.

In Figure 1, it can be seen that the curve for DOP lies below the
others, indicating that DOP has a lower vapor pressure at a given temperature
than the other materials shown. As the molecular weight increases in a family
of candidate chemical compounds, the vapor pressure decreases. Thus as the
carbon chain length in capric, lauric and myristic acids increases from C = 10 to
12 to 14, respectively, the curves in Figure 1 for these acids approach the lower
curve for DOP.

This simple analysis suggests that as the fatty acid carbon chain
length increases a better match is made with the vapor pressure characteristics
of DOP. Thus palmitic acid (C =16) or stearic acid (C = 18), which are not
shown in Figure 1, should most closely match DOP in this respect. But the
fatty acids just discussed are all solids at room temperature; their melting
points range from 31°C for capric acid to 68°C for stearic acid. As their vapor
pressure characteristics become more like those of DOP, they become increasingly

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Table 1. Comparisons of Physical Properties of Candidate Materials with DOP.

Properties	1st Choice	2nd Choice	3rd Choice
Vap Press	Tris 1.03	Hexa Gly 1.80	Bis 3.55
Vap Press, Viscosity	Tris 5.61	Seb 6.15	
Viscosity, Surf Tens	Tetra Gly 1.635	Seb 1.95	Oleic Acid 2.035
Viscosity, Boil Pt	Tetra Gly 1.50	Seb 1.96	Oleic Acid 2.06
Viscosity, Boil Pt, Density	Tetra Gly 1.53	Seb 1.965	Oleic Acid 2.08
Viscosity, Boil Pt, Density, Vap Press, Surf Tens, Mol Wt, Refr Index	Tris 5.64	Bis 6.285	
Viscosity, Surf Tens, Boil Pt	Tetra Gly 1.69	Seb 2.00	Oleic Acid 2.06
Viscosity, Surf Tens, Vap Press	Tris 5.615	Seb 6.20	

where:
Bis	= Bis (2-Ethylhexyl) Phosphate
Tris	= Tris (2-Ethylhexyl) Phosphate
Seb	= Di (2-Ethylhexyl) Sebacate (or "DOS", Dioctyl Sebacate)
Tetra Gly	= Tetraethylene Glycol
Hexa Gly	= Hexaethylene Glycol

Table 2. Best Fit Compounds for DOP

Properties	1st Choice	2nd Choice	3rd Choice
Normal Boiling Point	1-Octadecanethiol	Tris	Di Iso
Surface Tension	Bis	Oleic Acid	Di Butyl
Density	Di Iso	Bis	Di Butyl
Viscosity	Di Iso	Tris	Tetra Gly
Molecular Weight	Di Iso	Hexa Gly	Tris
Vapor Pressure	Diethyl Phthalate	Tris	Bis

where: abbreviations are as in Table 1, except:
Di Iso	= Diisooctyl Phthalate
Di Butyl	= Dibutyl Phthalate
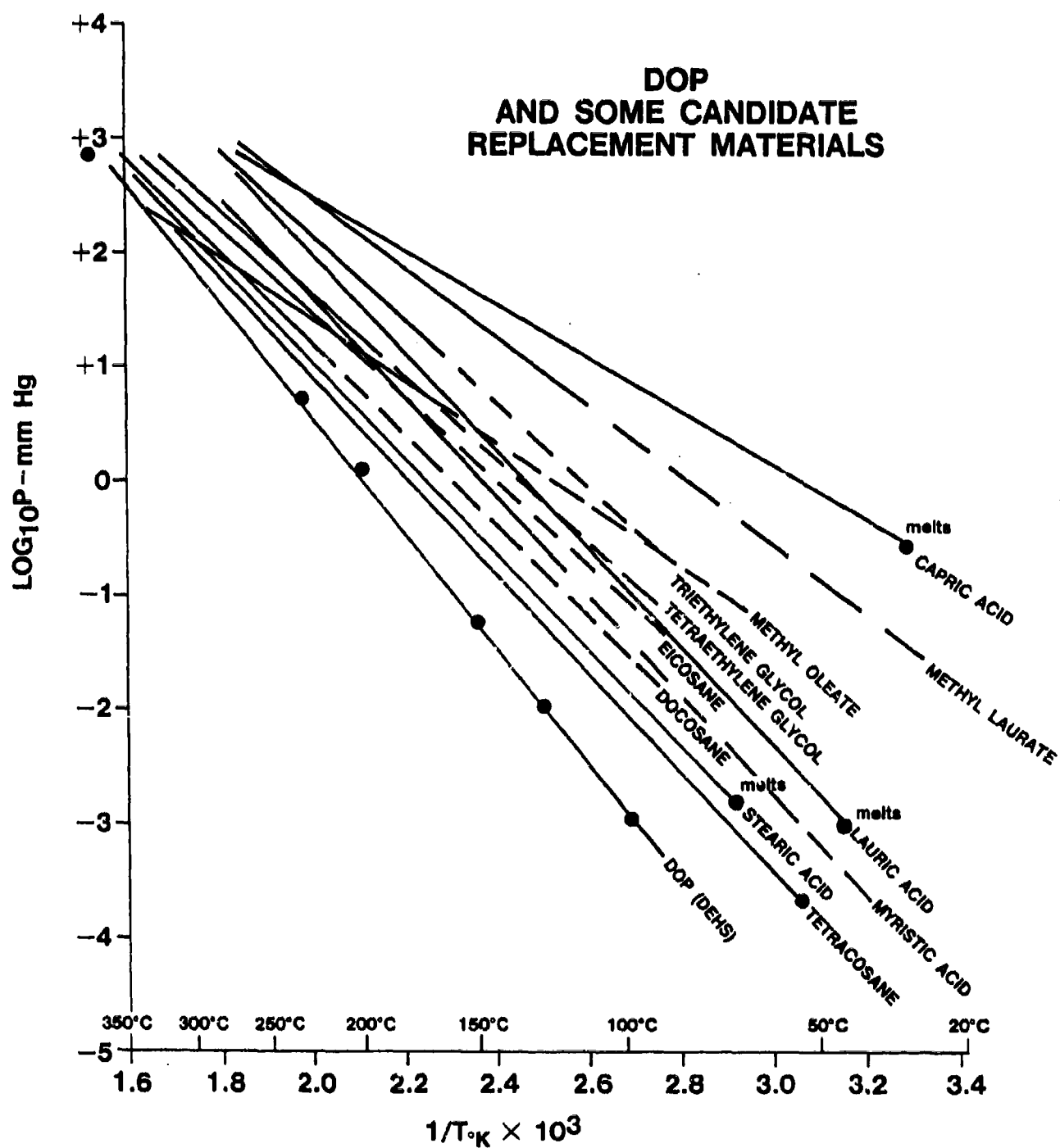
Figure 1. Clausius-Clapeyron Plot: DOP and Some Candidate
Replacement Materials.

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difficult to work with. They will melt in the Q127 machine pot and will vaporize, but the recondensation aerosols that they produce will become increasingly unpredictible with increasing chain length and melting point. They will not produce aerosols at all in the LAMAPP machine pot (Appendix E), which operates at room temperature.

It is much easier to work with candidate materials that are liquids at room temperature. But such materials usually have two characteristics that are undesirable:

●	they are unsaturated; i.e., they contain C:C double bonds that are sites for chemical attack leading to instability with aging, especially at elevated temperatures; rancidity and fungus growth could result;

●	their carbon chains are branched, rather than straight, as for the fatty acids just discussed; this increasingly complex structure increases the probability that human toxicological problems will be encountered in their use.

This analysis leads to the understanding that the search for materials to replace DOP will involve many compromises; indeed this is always the case when simulants are sought and used for any potentially toxic materials so that testing can be carried out safely.

Figure 1 suggests how compromises might be made to find a simulant for DOP to use in the Q127 machine. Suppose, for example, that the Q127 machine pot is normally maintained at 150°C (shown on the upper abscissa scale in Figure 1) when it contains DOP. This corresponds to an ordinate value of -1.3, or a DOP vapor pressure of 0.050 mm Hg. Moving horizontally to the right at the -1.3 ordinate value, we encounter the myristic acid curve at a temperature of about 100°C. This indicates that we should obtain the same vapor pressure with myristic acid at a pot temperature of about 100°C that we would obtain with DOP at 160°C.

There are other complications. For example, the Q127 machine pot temperature might not be conveniently adjusted to a temperature as low as 100°C. Even if this were possible, the acid might not recondense into an aerosol under conditions achievable using other Q127 machine settings, or it might not yield an aerosol with the specifications given here in Paragraph 1.2.1. Even if the acid works, it will still freeze during shut-down in the Q127 machine pot and fittings, because its melting point is 52°C. Its inhalation toxicological properties would still remain to be investigated.

In Paragraph 1.2.1. it was stated that the desired characteristics of a test aerosol are a CMD of 0.3μm, a target mass concentration of 100 mg/m^3, and a GSD (σ_g) equal to or less than 1.3. The mass concentration of an aerosol in milligrams per cubic meter is given by the equation:

$$mg/m^3 = \frac{\Pi}{6} \times 10^{-3} \, \rho \, N \, D^3_{\mu m} \tag{1}$$

where ρ is the density of the material, N is the aerosol particle population per cubic centimeter, and $D_{\mu m}$ is the particle diameter in micrometers. In Figure 2, Equation 1 is plotted for unit density spheres for the target CMD of $0.3\mu m$, and for two other particle diameters. It is seen that as the aerosol mass concentration approaches the target value of 100 mg/m^3, the number of $0.3\mu m$ particles per cubic centimeter approaches 7 x 10^6, and is well in excess of 10^7 for $0.2\mu m$ particles.

Populations as large as these exceed the operating range in which particle sizing spectrometers such as the LAS-X (Appendix E) operate quantitatively. For example, the LAS-X can count only 1.7 x 10^4 particles with 90% accuracy in a one cubic centimeter sample per second. Thus a dilution of several hundred times would be required to sample accurately the aerosol delivered to a Q127 machine canister test chuck at 100 mg/m^3. In the work reported here, such aerosol dilutions were made routinely using precision equipment.

A broader discussion of the physical property screening of candidate DOP replacement materials is given in Appendix H.

1.2.2.3 Candidate Material Costs and Other Factors.

All other factors are secondary to the toxicological properties of candidate replacement materials. The environmental hazards associated with the use of DOP have dictated the current problems which, in some cases, have actually closed down filter testing operations. Obviously, a successful replacement material must have acceptable toxicological properties and small environmental impact, regardless of the cost.

But cost becomes an important consideration if more than one replacement material for DOP can be found. If the competing materials are otherwise comparable in producing test smokes (aerosols) that meet the criteria of Paragraph 1.2.1 , and have acceptably low toxicities and environmental impact, cost could well become the deciding factor. A replacement material having a cost of about a dollar per pound, like DOP, could replace DOP in hundreds of penetrometer machines now operating worldwide with minimum economic impact.

Other factors which must be considered in choosing a material to replace DOP are:

• the impact of a new material upon existing testing hardware must be minimal;

• machine maintenance; it is undesirable to use a material that will clog the tester and/or will support fungus growth;

• destructive vs. non-destructive testing; DOP penetration testing is considered non-destructive, and a new material must also be non-destructive in the sense that it will not damage filters in standard test aerosol concentrations (even DOP might damage filters in massive concentrations);

• a new material must exhibit adequate stability and aging characteristics.

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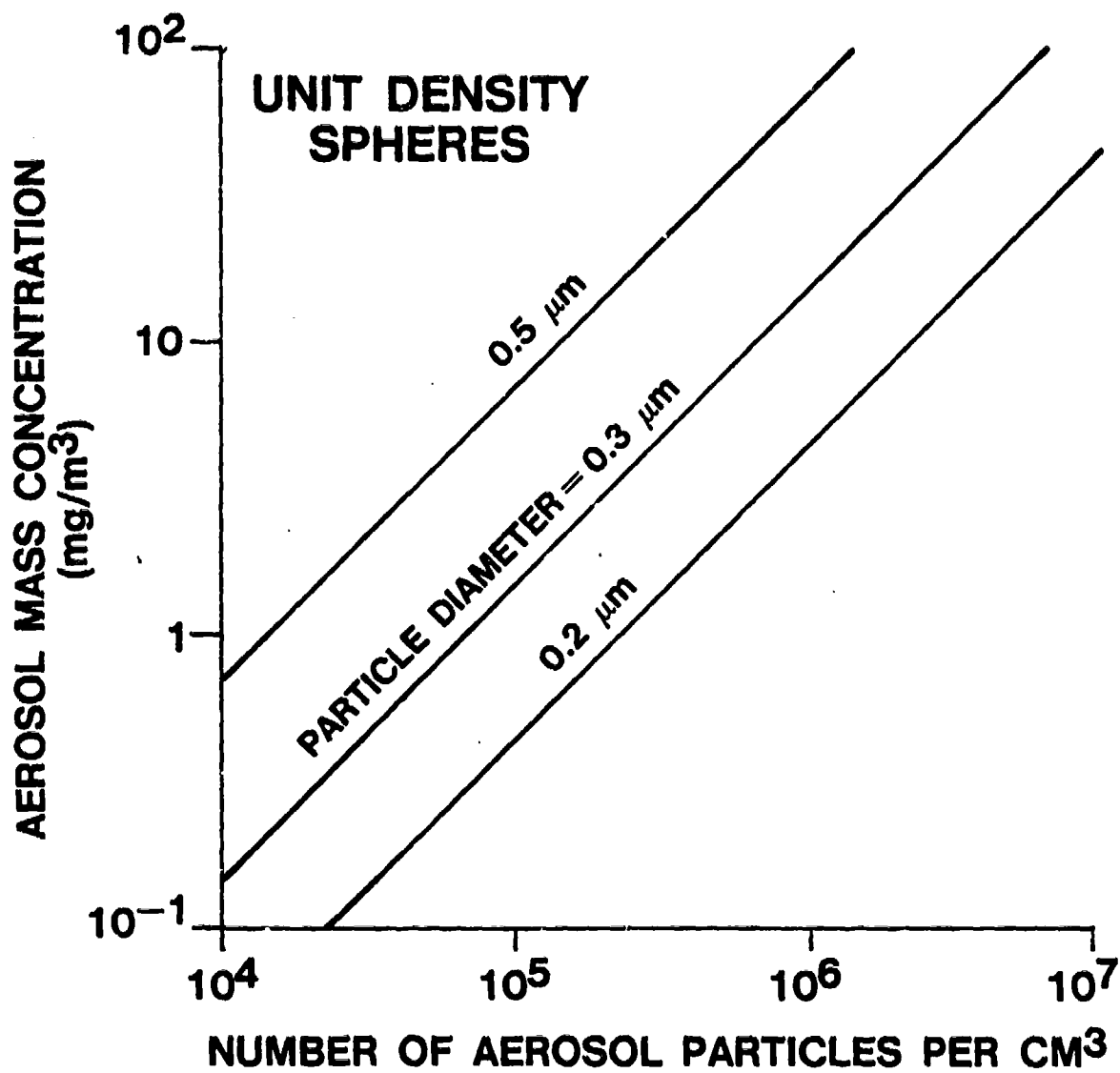
Figure 2. Plot of Equation 1 for Unit Density Spheres.

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Thus the selection of a successful replacement material for DOP, or the prioritization of usable materials if more than one is identified, is an exercise that can be facilitated by considering a matrix of properties like that shown in Table 3.

Table 3.   DOP Replacement Selection Matrix.

Selection Priority	Hypo- thetical Material	Toxicity?	How Well Does it Work in Testers?	Cost per Pound?
1.	A	very low	barely adequately	high
2.	B	low	adequately	very high
3.	C	borderline	very well	low
4.	D	significant	perfectly	very low

2.   EXPERIMENTAL FACILITY.

Bldg. E3348 in the Edgewood Area of Aberdeen Proving Ground was outfitted for the experimental investigations required in this program. A refurbished Q127 penetrometer machine (Appendix D) and the LAMAPP penetrometer (Appendix E) were set up side-by-side and were supplied by air from a nearby compressor. The air line was fitted with a refrigerative dehumidifier to remove moisture and other contamination, such as oil, from the air supplied to both machines.

Capillary diluters manufactured by TSI, Incorporated were used to sample aerosols from the Q127 machine to allow direct smoke analysis by the LAS-X Laser Aerosol Spectrometer (Appendix E), and direct comparison with aerosols from the LAMAPP machine.

The Model 3302 diluters were calibrated for dilution ratios of 100:1 and 20:1 at maximum flow rates of 5 standard lpm. Each diluter used a closed system employing filtered air from the original sample to mix with and lower the concentration of the aerosol at the output. The dilution air passed through two in-line HEPA filters.

The closed system preserved the integrity of the sample by maintaining the same relative humidity and elemental composition. Aerosol flow through the system was monitored by the pressure gradient across a capillary tube.

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LAS-X data from the Q127 machine were used as a standard from which particle size indications from the mechanical "Owl" could be assessed. Previously, an Owl reading of 29° had been used as an indicator of a 0.3 μm particle CMD for DOP. Since replacement candidate materials will give different Owl readings for this particle diameter (monitored by the LAS-X), the Owl reading for each usable candidate must be recorded so that Q127 machine operators in the field, not having access to a LAS-X system, can reproduce test aerosols having the proper specifications for filter quality testing.

A detailed Standard Operating Procedure (SOP) was prepared and staffed through the CRDEC Safety Office and other elements to permit machine operation with DOP and DOS (which was added to the list of suspected carcinogens after DOP was), as well as with candidate replacement materials. The SOP included a provision to age candidate samples in an oven at 140°C concurrently with their use in the penetrometer machines. In this way the stability and aging characteristics of promising candidate materials could be studied over periods ranging from weeks to months, even though their time of use in the machines would be limited to days because of the pressing schedule of candidate material testing.

3.   EXPERIMENTAL TEST PROCEDURE.

The LAMAPP machine has several operating adjustments which affect particle size distribution, these being the flow rates of the candidate material and of a salt solution (to produce condensation nuclei), the aerosol/dilution air flow ratio, and the evaporation tube temperature.

The LAMAPP machine has two nebulizers, one to generate the candidate material aerosol and one for the NaCl water solution that produces the nuclei. Particle size measurements were recorded using the printout feature of the HP-85 microcomputer (Appendix E) whenever the mean particle size and distribution were changed by varying the operating adjustments.

Candidate aerosols were first generated alone, without nuclei, and then with nuclei at gradually increasing concentrations until particle building became apparent. Candidate and NaCl concentrations were adjusted until a nominal particle size was achieved. Originally the evaporation tube temperature was set at 100°C, and this temperature was varied after the candidate material and NaCl solution flows were adjusted to achieve optimum particle distribution.

The evaporation tube temperature was monitored and was always kept well below the flash point of the candidate material. Dilution air flow was then varied to observe effects on particle size and distribution. Final readjustments of all parameters were made to achieve target particle size and distribution.

Aerosol concentrations were measured at the test chuck using preweighed filter paper inserted for five minutes at an air flow rate of 32 liters per minute.

The Q127 machine operating adjustments for particle size and distribution include the pot temperature, the quench air temperature, and the vapor pickup air/quench air flow ratio. The test aerosol concentration is

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also directly proportional to the pot temperature. Quench air entering the system was maintained at 25°C by a heat exchanger connected to a circulating water chilling system. Quench air temperature was then regulated in-line by a heating element controlled by a Variac variable transformer on the control panel, and the voltage setting corresponding to each air temperature was noted.

Vapor pickup and quench air flow rates were controlled by in-line flowmeters on the control panel. The ratio of quench air to vapor pickup air was shown to be optimal at 90:10 liters per minute; this ratio yielded the narrowest particle size distribution in most experiments. Given these flow rates, pot temperature and quench air temperature were the remaining particle size controlling parameters.

Candidate aerosols were initially generated at temperatures well below their flash points, usually at a pot temperature of 100°C. Concentration measurements were taken immediately using the technique described above for the LAMAPP machine.

The Q127 pot temp ture was then adjusted to produce a target concentration of aerosol near 100 mg/m^3, if achievable. Quench air temperature, for which the voltage was initially set at zero, was then increased until the target particle size was achieved. In general, the higher the quench air temperature, the larger the particles produced (see Table D.1 in Appendix D).

If particles were found to be too large at the initial control settings, the pot temperature was then raised, if possible without approaching the flash point of the candidate material, to raise the pot/quench air temperature ratio. This effect could also be produced by refrigerating the incoming quench air, but this would necessitate a major machine modification and was not considered desirable for this work.

Aerosol particle size and distribution were measured by diverting aerosol flow from the Owl optical chamber through the capillary diluter system (described in the previous section of this report) and into the LAS-X Laser Aerosol Spectrometer. Sampling was done downstream of the optical chamber to permit simultaneous readings to be made using the Owl and LAS-X instruments.

When the desired particle size and nominal distribution were achieved, the LAS-X output was recorded and the Owl reading was noted for future field operation of Q127 machines in filter testing with DOP replacement materials, as discussed previously. Several strip chart recorder printouts for DOP, DOS, and some candidate materials are displayed in Appendix I.

4.   CANDIDATE MATERIALS TESTED AND RESULTS.

4.1   General.

More than two dozen candidate materials were investigated as replacements for DOP in this research program. These are summarized in Tables 4 and 5, and will be discussed below. Selected but typical examples of experimental data and results for many different candidate materials are presented in Appendix I. The data tapes shown in Appendix I were obtained from the LAS-X/computer system (Appendix E); this system was used to sample aerosols from both the Q127 and LAMAPP penetrometer machines. Control settings of the Q127 machine that were required to produce suitable DOP replacement aerosols from promising candidate materials are shown in Table D.2. of Appendix D. Comparable settings of the LAMAPP machine are shown in Table E.1. of Appendix E.

4.2   Sources of Supply.

The candidate materials tested were obtained either directly from primary manufacturers, or from secondary suppliers whose unit prices ranged from five to ten times those of the manufacturers. The primary manufacturers, whose names are abbreviated in the tables and text of this report, and their products are as follows (other sources cited are secondary suppliers):

- Humphrey Chemical Company   Cosanes
  7621 Devine Street,
  P.O. Box 325,
  North Haven, Connecticut 06473

  Attn: Mr. Jim Humphrey
  1-(203)-281-0012

- Quantum Chemical Corporation   Synthetic
  Emery Division   Hydrocarbons
  Cincinnati Technical Center   (Poly-Alpha
  4900 Este Avenue,   Olefins)
  Cincinnati, Ohio 45232

  Attn: Mr. Fred Stroehlein
        Area Sales Representative
        1-(800)-543-7370
    or: Ms. Maureen J. Snyder
        Technical Service
        1-(513)-482-2100

- Quantum Chemical Corporation   Fatty Acids
  Emery Division
  1200 Route 46,   Fatty Acid Esters
  Clifton, New Jersey 07013
                                                Isostearic Acid
  Attn: Ms. Dee Williams
        Area Sales Representative
        1-(201)-773-1200

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- Witco Chemical Corporation   Fatty Acids
  Humko Chemical Division
  P.O. Box 125,   Fatty Acid Esters
  Memphis, Tennessee 38101

  Attn: Mr. Tom Brewer
        Area Sales Representative
        1-(901)-320-5941

- Witco Chemical Corporation   Petroleum Oils
  Sonneborn Division
  520 Madison Avenue,   White Mineral Oils
  New York, New York 10022-4236

  Attn: Mr. Bill Werner
        Area Sales Representative
        1-(212)-605-3981
    or: Mr. Paul Tietze
        Technical Services Manager
        1-(212)-605-3908

4.3   Available Toxicological Data.

The human toxicities of all candidate materials tested are
low according to Material Safety Data Sheets (MSDS) provided by the primary
manufacturers. For example, Quantum/Emery fatty acids and fatty acid
esters are made from natural oils and are not required to carry warning
labels, while their synthetic hydrocarbons (poly-alpha olefins) have been
FDA approved for indirect food contact. But the word "unknown" appears on
the MSDS for inhalation toxicity in almost every case where the entry is
not simply left blank, for these and some other materials.

Exceptions are the Humphrey MSDS for their cosanes which show,
for health hazards via the inhalation route of entry, "None, under normal
conditions" for n-octadecane (a solid), but "remove to fresh air" for n-
hexadecane (a liquid). Generally, the cosanes are stated to be mild
irritants, especially to sensitive skin, that can be decontaminated with
soap and water and, if ingested, can be diluted with 3-4 glasses of water
until the victim receives medical attention. Prolonged exposure is not
recommended.

MSDS for all of the candidate materials carry standard warnings
against use of inadequate ventilation and uncontrolled environmental
release, but no materials (except DOP and possibly DOS) have been assigned
occupational exposure limits including OSHA permitted exposure limits (PEL)
and/or American Conference of Governmental Industrial Hygienists (ACGIH)
threshold limit values (TLV).

For oleic acid, oleate esters, and isostearic acid, ingestion
LD50s of 20-50 milliliters per kilogram of body weight are typical in adult
rats. Mild conjunctivitis of the eye and mild skin irritation, with slight
erythema, are typical upon prolonged exposure to these materials.

The saturated straight-chain fatty-acids and fatty-acid esters
also have low toxicities. LD50s are in the range 10-20 grams per kilogram
or more, and eye and skin irritation are virtually nonexistant.

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The glycols exhibit very low toxicities. Apendix F contains a useful discussion of toxicological considerations of polyethylene glycols (PEGs), and physical properties of these compounds for several different carbon chain lengths. Some glycols have been shown to perform well as DOP replacement materials.

4.4   DOP: The "Standard" for Candidate Performance.

The performance criteria for successful candidate materials to replace DOP are clear: they must be toxicologically and environmentally innocuous when dispersed as aerosols, and they must have physical and chemical properties sufficiently similar to those of DOP to allow them to produce aerosols like DOP does when subjected to evaporation and recondensation in filter penetrometer testers like the Q127 machine.

Ideally, they should also work in machines that operate at room temperature using spray nozzles to evaporate a material which can then be recondensed on nuclei, for example, on NaCl nuclei as in the LAMAPP machine.

Appendix A gives detailed DOP data from Reference 1. Table D.2. in Appendix D gives Q127 machine settings for typical operation with DOP, and the ranges of CMD value, aerosol yield, and σ_g that result, for comparison with the candidate materials also shown there. Table E.1. in Appendix E gives similar information for typical operation of the LAMAPP machine.

Appendix I contains selected but typical statistical data for DOP from the LAS-X/computer system operated with either the Q127 machine or the LAMAPP machine.

4.5   Selected Candidate Replacement Materials.

About three dozen candidate materials were obtained from several suppliers including the primary manufacturers named in Section 4.2. These materials were either liquids or solids at room temperature. A test priority was established such that the materials were evaluated in the sequence:

- liquids in the Q127 machine;

- solids in the Q127 machine, in order of increasing melting point;

- liquids that produced aerosols like DOP does in the Q127 machine, evaluated in the LAMAPP machine;

- all other liquids in the LAMAPP machine.

Materials that are solids at room temperature were not evaluated in the LAMAPP machine because they could not be melted (as they are in the Q127 machine) and, consequently, they had vapor pressures too low to produce candidate aerosols.

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As is mentioned elsewhere in this report, it is possible that some solid materials, dissolved in suitable "inert" oils also investigated here, might allow operation of the LAMAPP machine using such solutions. But the evaluation of these techniques is beyond the scope of the present work.

4.5.1   Liquids at Room Temperature.

All liquids tested are summarized in Table 4, where typical performance data for the Q127 machine also are shown. Those liquids that produced usable DOP replacement aerosols in the Q127 machine are summarized in Table D.2. of Appendix D, with typical performance data and machine control settings. Liquids that produced usable DOP replacement aerosols in the LAMAPP machine are summarized in Table E.1. of Appendix E, with typical performance data and machine control settings.

4.5.2   Solids at Room Temperature.

All solids tested are summarized by increasing melting point in Table 5, where vapor pressures and flash points also are presented. Flash points become important when solids are heated in the Q127 machine "pot"; during testing the pot temperature was kept below the flash point of each candidate material to eliminate possible hazard to the machine operator.

In the present work, not all solid samples were tested (for reasons given in their discussion), and no solids were found to be suitable DOP replacement candidates.

4.5.3   DOS (Dioctyl Sebacate).

DOS can no longer be considered a candidate to replace DOP because DOS has also been added recently to the growing list of suspected carcinogens. It was included in this study because it is known to produce test aerosols which are comparable to those of DOP in both the Q127 and LAMAPP machines. Some typical data are shown in Appendix I.

DOS is di(2-ethylhexyl) sebacate. It has the same di(2-ethylhexyl) structure as DOP; it is an ester of sebacic acid, while DOP is an ester of phthalic acid. It is this common structure that appears to be implicated in the suspected carcinogenicity of both materials.

4.5.4   Cosanes.

The cosanes have the general structural formula:

$$CH_3-(CH_2)_{n-2}-CH_3$$
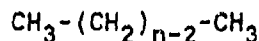
where n=16 for n-hexadecane, n=18 for n-octadecane, n=20 for n-eicosane, n=22 for n-docosane, and n=24 for n-tetracosane. Due to their simple straight-chain structure, the cosanes are relatively non-toxic and are comparable to other shorter-chain petroleum oil alkanes, such as those in gasoline and kerosene, in this respect. The candidate cosanes tested here were all solids at room temperature with the exception of n-hexadecane, which melts at 16°C.

Table 4. Summary of DOP Replacement Candidate Materials Tested, Ranked in Order of Probable Success; **Liquids**, **Q127 Machine**.

| Rank -ing* | Chemical Name | Manufacturer or Source | Trade Name | Typical Performance | | | Approx. |
				Range of CMD (μm)	Yield mg/m^3	σ_g	Cost,$/lb
1	"eicosane" (liquid)	Eastman Kodak Co.	unknown	.21-.30	87	1.25	unavail-able
2	isostearic acid (70-76%)	Emery Div., Quantum Chem.	Emersol 875	.20-.30	76	1.20-1.25	$ 1.51 (1 drum)
3	isostearic acid (60-66%)	Emery Div., Quantum Chem.	Emersol 871	.20-.30	85	1.20-1.25	$ 1.21 (1 drum)
4	synthetic hydrocarbon (80-85%)	Emery Div., Quantum Chem.	Emery 3004 4 CST Fluid	.20-.30	70-100	1.23	$ 0.90 (1 drum)
5	synthetic hydrocarbon (mixture)	Emery Div., Quantum Chem.	Emery 3006 6 CST Fluid	.19-.21	110	1.20	$ 0.90 (1 drum)
6	oleic acid (71%)	Humko Chem. Div., Witco	Industrene 206LP	.19-.30	66-200	1.28-1.30	$0.90 (1 drum)
7	oleic acid (74%)	Emery Div., Quantum Chem.	Emersol 233 LL	.19-.30	75	1.25-1.40+	$ 0.88 (1 drum)
8	methyl oleate (69%)	Humko Chem. Div., Witco	Kemester 105	.26-.32	698	1.38	$ 0.91 (1 drum)
9	synthetic hydrocarbon (99%)	Emery Div., Quantum Chem.	Emery 3002 2 CST Fluid	0.3-	390	1.40	$ 0.90 (1 drum)
*	n-hexadecane tech.gr.(90%)	Humphrey Chem. Co.	A-16				$ 1.70 (1 drum)
*	" (pure: 99%)**	"					$15.12 (0.75 kg)
*	methyl oleate stearate (58/24%)***	Emery Div., Quantum Chem.	Emery 2219				$ 0.68 (1 drum)
*	methyl laurate (96%)	Emery Div., Quantum Chem.	Emery 2296				$ 1.06 (1 drum)
*	methyl myr-istate (95%)	Emery Div., Quantum Chem.	Emery 2214				$ 1.11 (1 drum)

Table 4. (Continued)

*	oleic acid (71%)	Humko Chem. Div.,Witco	Industrene 206 LP		$ 0.91 (1 drum)
*	white mineral oil (37% C15, 25% C16)	Sonneborn Div., Witco	PD23		
*	white mineral oil (25% C16, 40% C17)	Sonneborn Div., Witco	PD25		
****	hexaethylene glycol	Parrish Chem. Co.	Cat. No. 2264		$545.60 (1 kg)
*	tetraethylene glycol				
*	polyethylene glycol				

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* Highest rankings have highest probability of success; if not ranked (asterisk shown), not considered a viable DOP replacement candidate.
** This material not at CRDEC for testing.
*** Material is 58% methyl oleate and 24% methyl stearate mixture.
**** A usable candidate, but cost is prohibitive.

Table 5. Summary: Samples of **Solids** Available for Test as DOP Replacement
Candidate Materials; Listed **by Increasing Melting Point**.

Melting* Point,°C	Chemical Name	Manufacturer or Source	Trade Name	Vap. Press. mm Hg @ °C	Flash Pt.,°C	Approx. Cost,$/lb
27	methyl palm- itate (95%)	Emery Div., Quantum Chem.	Emery 2216	1 @ 137 2 @ 148 10 @ 184 15 @ 196 747 @ 417	165	$ 0.98 (1 drum)
28	n-octadecane tech.gr.(90%)	Humphrey Chem. Co.	A-18	10 @ 173.5 760 @ 316	165	$ 1.70 (1 drum)
"	" (pure: 99%)**	"		"		$ 13.91 (0.75 kg)

(continues)

Table 5. (Continued)

32	methyl stear-ate (90%)	Humko Chem. Div., Witco	Kemester 9018	15 @ 214.5 less than 760 @ 260	166	
36	methyl stear-ate (95%)	Emery Div., Quantum Chem.	Emery 2218	1 @ 158 10 @ 206	153	$ 1.06 (1 drum)
36	n-eicosane (99%)**	Humphrey Chem. Co.	A-20	.00013 @ 20 (est) 14 @ 200		$ 24.19 (0.75 kg)
43	lauric acid (95%)	Humko Chem. Div., Witco	Hystyrene 9512	1 @ 131 100 @ 225	158	
44	n-docosane (99%)**	Humphrey Chem. Co.	A-22	.00003 @ 20 (est) 6 @ 200		$ 38.10 (0.75 kg)
44	n-docosane (99%)	Sigma Chem. Co.	D-4509	as above		$126.50 (1 kg)
51	n-tetracosane (99%)**	Humphrey Chem. Co.	A-24	.000006 @ 20 (est) 3 @ 200		$ 64.70 (0.75 kg)
51	n-tetracosane (99%)	Sigma Chem. Co.	T-4758	as above		$249.40 (1 kg)
52	myristic acid (90%)	Humko Chem. Div., Witco	Hystyrene 9014	1 @ 149 100 @ 250.5	177	
55	stearic acid (45.5%), pal-mitic (50%)	Emery Div., Quantum Chem.	Emersol 132 NF LILY	1 @ 180	196	$ 0.63 (200-999 lb)
60	palmitic acid (92%)	Humko Chem. Div., Witco	Hystyrene 9016	100 @ 270 760 @ 390	188	
67	stearic acid (95%)	Humko Chem. Div., Witco	Hystyrene 9718	15 @ 232 110 @ 291 760 @ 360	202	
68	stearic acid (90%)	Emery Div., Quantum Chem.	Emersol 152 NF	10 @ 225	185	$ 0.71 (200-999 lb)
68	stearic acid (95%)	Emery Div., Quantum Chem.	Emersol 153 NF	10 @ 225	185	$ 0.72 (200-999 lb)

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* Operational problems increase as melting point increases above ambient.
** This material not at CRDEC for testing.

4.5.4.1 Mixed Fractions: Petroleum Oils.

The physical properties of mixtures of petroleum oil and cosane fractions depend upon their carbon-chain lengths and the relative abundance of individual fractions, and upon whether their molecules have branched or straight carbon chains. Branched-chain molecules have lower melting points than straight-chain molecules; hence they are generally liquids at room temperature.

The general structural formula given above for the cosanes is that of straight-chained molecules. But there is no prima facie reason why branched-chain, saturated oils might not also work in the penetrometer machines. And, they would have the advantage of being liquids at room temperature.

Two white petroleum or mineral oil samples were evaluated in this work, designated Sonneborn PD23 and PD25 (see Table 4). PD23 comprises 9% C13, 21% C14, 37% C15, and 25% C16. Its pour point is -21°C, its flash point is 107°C, and its specific gravity is 0.80-0.81.

PD25 comprises 25% C16 and 40% C17, with lesser fractions of other carbon-chain lengths. Its pour point is -1°C, its flash point is 124°C open cup, and its specific gravity is 0.80-0.81.

These candidate materials were unsuccessful in the LAMAPP machine. For example, PD23 yielded aerosols whose size and distribution were very difficult to control.

Neither PD23 nor PD25 performed well in the Q127 machine. Their relatively high volatilities prevented them from recondensing reliably into smokes, but they tended instead to recondense on cool, interior surfaces of the machine thus leading co fouling and the need for cleaning before further candidate materials could be tested.

This does not preclude their possible use, however, in "cold" machines where they could be sprayed in a broad size distribution for testing such as that now being carried out using, for example, corn oil.

4.5.4.2 n-Hexadecane.

This material is a colorless liquid at room temperature, with a slight odor. It melts at 18°C and has a flash point of 135°C. Our sample was at least 90% pure, and had a vapor pressure of less than 1 mm Hg at 20°C. Its specific gravity was 0.773.

n-hexadecane did not perform well in the Q127 machine. Its behavior was much like that of the petroleum or mineral oils just discussed. It produced little or no smoke, and recondensed in the Owl, forming droplets and fouling optics. It gave a σ_g of 1.3+ and a mean particle size of about 0.18 μm, with a yield of 415 mg/m^3.

n-hexadecane was not tested in the LAMAPP because of the recondensation problems encountered in the Q127 machine and the availability of good candidates for LAMAPP that had already been tested. However, this material could be evaluated for future applications if necessary.

4.5.4.3 n-Octadecane.

This material is a white solid at room temperature, with a slight odor. It melts at 28°C and has a flash point of 165°C. Our sample was at least 90% pure. It had a vapor pressure of less than 1 mm Hg at 20°C, and a specific gravity of 0.77.

n-octadecane also did not perform well in the Q127 machine, although it is less volatile than n-hexadecane. CMD could not be controlled by the operator, and varied over the range $0.4-1.0\mu m$, with a σ_g range of 1.3-1.5. This material was not tested in the LAMAPP machine since it is a solid at room temperature and LAMAPP has an unheated "pot".

4.5.4.4 n-Eicosane.

The sample of "n-eicosane" that we tested worked extremely well in the Q127 machine, producing smokes with CMDs adjustable over the range $0.15-0.30\mu m$, and σ_gs as low as 1.15. But our sample, from Eastman Kodak Co., was a liquid at room temperature whereas pure n-eicosane has a melting point of 36°C. This paradox could not be resolved by Kodak representatives, since that supplier no longer markets this material.

A portion of our sample was sent for analysis to the Humphrey Chemical Co., a manufacturer of cosanes from which Kodak had obtained its earlier supplies for repackaging. The analysis showed that our sample comprised only about 14% n-eicosane, but more than 60% of tetracosane (C24) that was extensively branched rather than being straight-chained. This was thought to have come from a Venezuelian oil source about which little information survives.

The success of this sample suggested that it might be very worthwhile to experiment with <u>solutions of candidate materials in suitable oils with sufficiently different molecular weights such that promising candidates could be utilized at room temperature where they would otherwise be solids</u>. Such investigations appear to deserve further attention.

Pure n-eicosane is a solid at room temperature with a specific gravity of 0.79. It has a vapor pressure of about 13×10^{-5} mm Hg at 20°C, and about 14 mm Hg at 200°C. Due to uncertainties about the sample and its limited quantity, and the fact that pure n-eicosane is a solid at room temperature, this material was not tested in the LAMAPP machine.

4.5.4.5 n-Docosane.

This material is a solid at room temperature, with a melting point of 44°C and a specific gravity of 0.79. It has a vapor pressure of about 3×10^{-5} mm Hg at 20°C, and about 6 mm Hg at 200°C. Our test sample was 99% pure.

Because of the performance of good candidate materials that are liquids at room temperature, for both the Q127 and LAMAPP machines, plus testing problems encountered with the cosanes generally, n-docosane was not evaluated, but is available for future evaluation if necessary.

4.5.4.6   n-Tetracosane.

Pure n-tetracosane is a solid at room temperature, melting at 51°C, with a specific gravity of 0.80. Its vapor pressure is about 6×10^{-6} mm Hg at 20°C, and about 3 mm Hg at 200°C. The sample that we tested was 99% pure.

This material was not evaluated in either the Q127 machine or the LAMAPP machine, for the same reasons indicated for n-docosane in the previous section of this report.

4.5.5   Synthetic Hydrocarbons.

Synthetic hydrocarbons include poly-alpha olefins (PAOs), which are used as synthetic lubricants and in other applications. These versatile, saturated, synthetic hydrocarbons are produced by direct oligomerization of decene-1. Linear alpha olefins are polymerized and hydrogenated to manufacture PAOs. Three PAOs were investigated in our studies; these are designated Emery 3002, 3004 and 3006. Data are summarized in Table 6.

Table 6.   Properties of Poly-Alpha Olefins (PAOs).

Trade Name	Pour Point, °C	Flash Point, °C	Fire Point, °C	Auto-Ignition Point, °C	Specific Gravity
Emery 3002	-65	164	178	324	0.80
Emery 3004	-69	225	250	343	0.82
Emery 3006	-64	243	266	371	0.83

In the Q127 machine, Emery 3004 performed best, giving a CMD adjustable from 0.2 to 0.3µm, with a σ_g of 1.23 and an adequate aerosol yield. The "pot" temperature was 180°C. Emery 3002 was too volatile, and produced large aerosol yields that could not be adjusted to CMDs below 0.3µm and which had σ_g values of 1.40-1.67 or more. Emery 3006 had to be heated to 195°C to yield 110 mg/m^3 of aerosol with a σ_g value of 1.20, but the CMD could not be adjusted above 0.21µm, and a strong odor was given off.

In the LAMAPP machine, Emery 3002 performed very well, giving a CMD range of 0.18-0.28µm, σ_gs of 1.18 at CMD = 0.20µm and 1.30 at 0.28 µm, and an aerosol yield of 32 mg/m^3. Emery 3004 was less successful in the LAMAPP machine, giving a 0.18-0.23µm CMD range and a yield of 26 mg/m^3, but with a σ_g of 1.32 at a CMD of 0.20µm. Emery 3006 was unsuccessful because of its low vapor pressure.

4.5.6   Fatty Acids.

"Fatty acids" here include straight-chain and branched, saturated compounds, and compounds whose molecules contain one or more double bonds. Branched, saturated materials like isostearic acid are liquids at room temperature, as are many materials such as oleic acid that contain double bonds. Straight-chain, saturated fatty acids range from liquids at lower molecular weights to waxy solids at higher molecular weights at room temperature.

4.5.6.1 Oleic Acid.

Oleic acid has the structural formula:

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$$
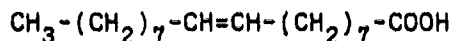
where one double bond exists between the ninth and tenth carbons of an 18-carbon chain. The molecule is most easily chemically attacked at this double bond, making this acid less stable during aging at elevated temperatures than saturated fatty acids. Nevertheless, it performs well in the Q127 machine with the exception that the aerosol concentration and σ_g are sometimes difficult to control (see Table D.2. in Appendix D). Similar data for the LAMAPP machine are given in Table E.1 of Appendix E. Oleic acid gave promising performance in the LAMAPP machine, but was not fully evaluated due to scheduling conflicts and thus, is not recommended as a DOP replacement material for LAMAPP in this report, pending further testing.

The oleic acid used here was 71-74% pure, with the remainder consisting mainly of palmitoleic and linoleic acids, in that order. It is a light yellow liquid at room temperature, with a slight odor. It melts at 11-14°C, and has a vapor pressure of 10 mm Hg at 224°C. Its flash point is approximately 184-189°C closed cup, and 193°C open cup.

4.5.6.2 Isostearic Acid.

Isostearic acid has the structural formula:

$$CH_3-\overset{\displaystyle CH_3}{\overset{\displaystyle /}{C}H}-(CH_2)_{14}-COOH$$
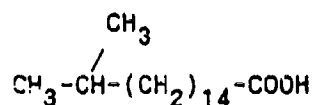
where the single-branched methyl group usually occurs in the position shown but also ca, occur at any other position along the carbon chain with a much lower probability.

Thus it is an isomer of stearic acid, discussed below, but the two acids have distinctly different physical properties. Isostearic acid is a light yellow liquid at room temperature with a melting point of 12-15°C, depending upon its purity, and it has a vapor pressure of 50 mm Hg at 265°C. Its flash point is approximately 182°C open cup.

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Two samples of differing purity were used in this work. The purest sample was 70-76% isostearic acid, with the remainder consisting of myristic, isopalmitic, and palmitic acids, in that order. The less pure sample was 60-66% isostearic acid, with the remainder consisting of isooleic, oleic, stearic, and isopalmitic acids, in that order.

Both samples worked very well in the Q127 machine, with the purer material yielding slightly higher aerosol concentration. This can be observed in Table D.2. of Appendix D. Isostearic acid also worked quite well in the LAMAPP machine (see Table E.1. in Appendix E). Thus it appears to be an excellent candidate to replace DOP in the Q127 and LAMAPP machines.

The oxidation stability of isostearic acid appears to be excellent compared to other candidate materials. A standard sample required 100 days to absorb 10 ml of oxygen at 60°C, while under the same conditions commercial oleic acid required only 1-7 days and glyceryl trioleate required only 5 hours.

4.5.6.3 Stearic Acid.

The saturated straight-chain fatty acids have the general structural formula:

$$CH_3-(CH_2)_{n-2}-COOH$$
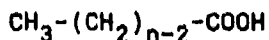
where n=18 for stearic acid. Three samples of this waxy, white solid were used in this work; one each of 90% and 95% purity from one manufacturer, and one of 95% purity from a second manufacturer. The remainder of each sample consisted almost entirely of palmitic acid. Stearic acid melts at 67-68°C, which is easily accomodated by the Q127 machine, but is extremely difficult to work with since it freezes in the machine "pot" during shutdown and is difficult to remove from plumbing external to the pot. It was the highest-melting of any candidate material tested; thus these problems were worse than would be expected for lower-melting materials (or, of course, liquids).

Some vapor pressures for stearic acid, in mm Hg, are as follows for the temperatures indicated: 10 at 225°C; 15 at 232°C; 110 at 291°C; 760 at 360°C. Its flash point is is 185°C open cup.

Stearic acid performed poorly in the Q127 machine. It produced a very fine aerosol of approximately 0.1μm CMD at very low concentration, with a narrow σ_g of 1.12 (one of the lowest ever recorded). But this was accompanied by large concentrations of "snowflakes" that threatened to foul the Q127 machine and its instrumentation. When the quench air temperature was increased, the CMD increased to 0.3μm or more, but σ_g also increased to more than 1.40.

Because the LAMAPP machine pot operates at room temperature it was not possible, of course, to evaluate solid candidate materials in that machine. This does not rule out the possibility that some solid candidate

materials, dissolved in suitable liquids, can be evaluated using the
LAMAPP system in future research investigations. In the investigations
discussed in the present report, the LAMAPP system was evaluated using
only liquid candidate materials.

4.5.6.4 Palmitic Acid.

Palmitic acid has the structure shown in the general formula imme-
diately above, where n=16. The material used was 92% pure, with impurities
of 7% stearic and 1% myristic acids. Palmitic acid melts at 60°C, and is a
white-to-tan solid at room temperature. Its vapor pressure is 100 mm Hg at
270°C and 760 mm Hg at 390°C. Its flash point is approximately 188°C open
cup.

Because of the problems encountered in operating the Q127 machine
with stearic acid, palmitic acid and the other (solid) acids in this series
were not evaluated in the present program after it became apparent that
good liquid candidate materials were available. As solids, these materials
were not tested in the LAMAPP machine either.

4.5.6.5 Myristic Acid.

Myristic acid has the structure shown in the general formula
above, where n=14. The material used was 90% pure, with impurities of 6%
palmitic and 4% lauric acids. Myristic acid melts at 52°C, and is a white-
to-tan waxy-solid at room temperature. Its vapor pressure is 1 mm Hg at
149°C and 100 mm Hg at 250.5°C. Its flash point is approximately 177°C
open cup.

Testing of this material was not carried out in the present pro-
gram with either machine, for the reasons given in Paragraph 4.5.6.4.

4.5.6.6 Lauric Acid.

Lauric acid has the structure shown in the general formula above,
where n=12. The sample used was 95% pure, with impurities of 3% myristic
and 2% capric acids. Lauric acid melts at 43°C, and is a white-to-tan,
free-flowing solid at room temperature. Its vapor pressure is 1 mm Hg at
131°C and 100 mm Hg at 225°C. Its flash point is approximately 158°C open
cup.

Testing of lauric acid was not carried out in the present
program with either machine, for the reasons given in Paragraph 4.5.6.4.

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4.5.7   Fatty Acid Esters.

The methyl esters of oleic acid and several saturated, straight-chain fatty acids were evaluated, with the following results.

4.5.7.1   Methyl Oleate.

Methyl oleate has the structural formula:

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COO-CH_3$$
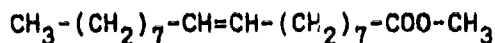
where one double bond exists in the position shown. Our sample was 69% pure, with linoleic and palmitoleic acids being the main impurities. The manufacturer gives no melting point, but methyl oleate is a light yellow liquid with a slight odor at room temperature. The flash point is approximately $163^\circ C$ open cup.

This material produced smoke in the Q127 machine over the CMD range $0.20-0.30\mu m$, but the distributions were fairly broad with σ_gs of about 1.30. A large, variable yield was observed: 66-206 mg/m^3. See Table D.2. in Appendix D.

In the LAMAPP machine, this material was moderately successful. It produced a σ_g of 1.24 at 0.2 μm mean particle diameter, but σ_g rose to 1.45 at a mean diameter of 0.3 μm. The smoke concentration at the chuck was 35 mg/m^3.

4.5.7.2   Methyl Oleate Stearate.

Methyl oleate stearate is a mixture of 58% methyl oleate, whose structural formula is shown immediately above, 24% methyl stearate, whose structural formula is shown below where n=18, 14% methyl linoleate, and 4% methyl palmitate (n=16 in the formula below).

It melts at $18^\circ C$, and is a light yellow liquid. Its vapor pressure is 10 mm Hg at $205^\circ C$, and its flash point is approximately $173^\circ C$ open cup.

This material produced a thin smoke in the Q127 machine that could not be read by the Owl. The CMD range was $0.24-1.1\mu m$, and the σ_g range was 1.4-1.5. In the LAMAPP machine, this material performed successfully. σ_g was 1.22 at 0.22 μm mean particle diameter, and 1.20 at 0.30 μm mean diameter.

4.5.7.3   Methyl Stearate.

The saturated straight-chain methyl esters have the general structural formula:

$$CH_3-(CH_2)_{n-2}-COO-CH_3$$

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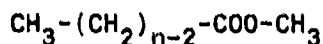
where n=18 for methyl stearate. Two samples were obtained. The first was 95% pure with impurities of 4% methyl palmitate and 1% methyl oleate. The second sample was 90% pure with 10% palmitic esters as impurities. Methyl stearate melts at 32-36°C. It is a white solid with a vapor pressure of 10 mm Hg at 206°C. Its flash point is 153-166°C closed cup.

Due to scheduling difficulties, methyl stearate was not tested in either machine during the present program. Preference was given to lower-melting materials in the Q127 machine, as discussed below.

4.5.7.4 Methyl Palmitate.

Methyl palmitate has the structure shown in the general formula immediately above, where n=16. Our sample was 95% pure, with impurities of 3% methyl stearate and 2% methyl myristate. This white solid melts at 27°C, has a vapor pressure of 10 mm Hg at 184°C, and has a flash point of 165°C open cup.

Because of scheduling priorities, methyl palmitate was not tested in either machine during the present program, preference being given to the lower-melting (liquid) materials discussed in the next two sections.

4.5.7.5 Methyl Myristate.

Methyl myristate has the structure shown in the general formula above, where n=14. The sample evaluated was 95% pure, and was a liquid at room temperature with a melting point of 18-19°C. Its vapor pressure was 7 mm Hg at 156°C and 751 mm Hg at 295°C. The manufacturer gives no flash point.

This material recondensed in the Owl when used in the Q127 machine, and the smoke could not be read by the Owl. At a pot temperature of 156°C, the aerosol yield was very large (2800 mg/m^3) and the CMD covered the range 0.27-0.45μm. But the σ_g ranged from 1.7 to 2.5.

This material was unsuccessful in the LAMAPP machine. Particle size was difficult to control, and the size distribution was often too broad. The mean particle size was less than 0.18 μm, and σ_g ranged from 1.16 to 1.50, with an aerosol yield of about 219 mg/m^3.

4.5.7.6 Methyl Laurate.

Methyl laurate has the structure shown in the general formula above, where n=12. The sample evaluated was a water-white liquid at room temperature with a melting point of 5°C, and was 96% pure. The impurities were 2% each of methyl myristate and methyl caprate. The sample vapor pressure was 10 mm Hg at 160°C and 20 mm Hg at 190°C. The flash point was 152°C, closed or open cup.

This material also recondensed in the Owl, yielding a weak smoke in the Q127 machine. The range of CMD was 0.20-0.49μm, and of σ_g 1.4-1.6. In the LAMAPP machine, the material was unsuccessful because particles could not be built to the proper size, and the distribution was very broad. The mean particle diameter was as large as 0.26 μm, but σ_g was greater than 1.40 with an aerosol yield of about 208 mg/m^3.

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4.5.8   Polyethylene Glycols (PEGs).

The polyethylene glycols have the general structural formula:

$$HO-(CH_2-CH_2-O)_n-H$$
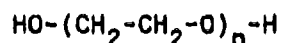
where n=4 for tetraethylene glycol, and n=6 for hexaethylene glycol; these were the glycols evaluated in this program. Gerber[2] also made a detailed study of pentaethylene glycol (n=5) in Q127 machines. His results are presented in detail in Appendix F, which contains toxicological information concerning the glycols as well.

4.5.8.1   Mixed Fractions.

Polyethylene glycol (PEG) mixtures are identified by their average molecular weight which typically is specified as 200, 300, 400, 600, 1000, and so forth. For example, PEG 200 contains about 22% n=4, 21% n=5, and 15% n=6. PEG 600 contains about 11% each of n=12,13,14, and 15.

Mixtures are troublesome in penetrometer machines using "monodispersed" aerosols because each glycol fraction has its own characteristic physical properties, including vapor pressure, compared to its neighbors at adjacent "n" numbers. Thus each fraction, if evaporated, will recondense into aerosol particles having somewhat different CMDs than those of neighboring fractions. The result is a broadening or "smearing" of GSD (σ_g) for the entire aerosol distribution, and this is contrary to the desired monodispersity.

If PEGs are purified to be made 90-plus percent pure in one "n" number, their manufacturing cost increases dramatically. Gerber[2] has discussed this (Appendix F). Otherwise, pure glycols appear to be very promising candidates. Glycols are used in pharmaceuticals and cosmetics, and as direct food additives, suggesting that their toxicological properties are among the most desirable of the candidate materials considered here.

A possible problem with the glycols as replacement materials for DOP is their hygroscopicity; they are infinitely miscible with water. Thus it is possible that under unusual conditions of humidity, the test aerosol produced can be affected if reasonable operating precautions are not taken.

4.5.8.2   Tetraethylene Glycol.

Tetraethylene glycol melts at -6.2°C, has a density of 1.1285 at 15°C, and has vapor pressures of 14 mm Hg at 198°C and 760 mm Hg at 328°C.

In the Q127 machine, this material was difficult to control and gave broad size distributions. Typical σ_g was greater than 1.40, with mean diameters of about 0.3 to 0.65 μm. Better control might have been possible using refrigerated input air. Tetraethylene glycol is too volatile to perform well under typical Q127 machine operating conditions, and it was not evaluated in the LAMAPP machine.

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4.5.8.3 Hexaethylene Glycol.

Gerber[2] proposed the use of hexaethylene glycol in Q127 machines as a safe replacement material for DOP (see Appendix F). It is very expensive (see Table 4), but should have the proper range of vapor pressure to perform well in DOP replacement applications, as explained in Appendix F.

This material was not tested for a variety of reasons, including the following: (1) much cheaper, promising candidates were identified; (2) contamination of the small, expensive sample would have rendered it unfit for careful future investigations; (3) this material was intended to be tested last among the candidates, by which time the CRDEC Safety Office had virtually shut down all penetrometer testing by withholding approval of a Standard Operating Procedure (SOP).

5. OTHER CANDIDATE MATERIALS.

5.1 Polyethylene Glycol Diesters.

The general structural formula for polyethylene glycol diesters is:

$$RCO-O-(CH_2-CH_2-O)_n-COR$$
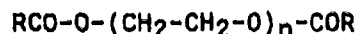
where R is the radical corresponding to the acid diester of interest. For example, R is the methyl radical or group CH_3 in the case of acetic acid, for which the diester formed would be tetraethylene glycol diacetate if n=4.

These materials are not readily available commercially, and must be synthesized by acidification of the polyethylene glycol of choice. They are more costly than other candidate materials because they must be synthesized, and their physical properties are not generally known. When determined, they are found not to differ greatly from those of the parent glycol.

For example, diethylene glycol diacetate (n=2 in the formula above) has virtually identical vapor pressure and density as those of diethylene glycol itself. Triethylene glycol diacetate (n=3 above) has a slightly lower vapor pressure than that of pure triethylene glycol. Increasing the size of the radical R would tend to change the properties of the diesters compared to those of the parent glycols, but this would also complicate the molecular structure which could increase the toxicity of the material.

Quantities of tetraethylene glycol were procured during this program so that candidate tetraethylene glycol diesters could be synthesized at CRDEC for evaluation, if necessary. However, promising results with other candidate materials, combined with marginal changes in the physical properties of the diesters compared to tetraethylene glycol itself, precluded the synthesis and evaluation of the diesters during the present effort.

5.2   Other Materials.

Several other possible candidate materials were mentioned in the ESP and were noted in the Test Plan (Appendix C). These included erythritol, pentaerythritol, and glyceryl stearate (a wax). Corn oil specifically was not to be evaluated because of its tendency to become rancid during use (its carbon chains are unsaturated and, hence, are subject to chemical attack at the double bonds). These materials were not tested because of the promise of other candidate materials, and because of their relative molecular complexity suggesting toxicological unsuitability.

There are many kinds of mineral or petroleum oils on the market that could have been tested. These include Nujol, which is widely used by spectrocopists, and materials such as "Nor Par" and the "Iso Nor Pars" which are reported to be manufactured by the Exxon Corporation and are highly branched. Our own results with the mixed fraction petroleum oils including PD23 and PD25 (Section 4.5.4.1.) in the Q127 machine were not promising, and it is unlikely that other similar oils would succeed either. Attention is better focused on the PAOs and the cosanes.

6.   DISCUSSION.

6.1   General.

The calibration of the LAS-X Laser Aerosol Spectrometer used in this work, and LAS-X limitations, are not trivial. They deserve serious attention in all future efforts where precision measurements in support of filter penetrometer testing are required   These aspects are discussed in detail in Appendix J. As longer-term improvements are made to the Q127 machine, and as the LAMAPP machine and similar systems are developed to meet production quality assurance needs, engineers must be completely familiar with modern optical particle-sizing theory and techniques.

6.2   Use of Replacement Materials in the Q127 System.

Ideally, DOP could be drained from the "pot" of any Q127, or similar "hot" machine presently in day-to-day operation, and an innocuous replacement material could be poured in, thus allowing routine operation to continue pending final approval of the material by the Surgeon General and/or other authorities. Some of the materials recommended in this report appear to have that potential. But even if this should occur, updating of Q127 and similar hot machines in the field still deserves high priority. In other words, if a successful replacement material for DOP is found, this does not preclude the need to modernize aging machines currently in use.

6.3   Longer-Term Improvements to the Q127 System.

The research reported here was deliberately carried out with only minor modifications being made to our Q127 machine, which otherwise was operated at room temperature and without cooling water being used in the heat exchanger, or any other special provisions. The intent was to provide one or more replacement materials that could simply be placed in existing Q127 machines, and similar "hot" machines, in the field without the need for further modification.

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If a successful replacement for DOP is found and is proven in first trials with machines in the field, it will be very worthwhile to consider how longer-term improvements might be made to these machines to further improve their reliability and reproducibility of operation. These improvements could be accomplished without significant mission interruption through one or more field retrofits.

Several improvements to existing Q127 machines that have suggested themselves in this work include: provision of all-solid-state electronics; provision of a modern version of the LAS-X to replace the Owl; provision of a modern photometer; provision of a digital, programmable temperature controller for the "hot pot"; replacement of the copper-containing heating coil in the hot pot with one of inert metal; replacement of asbestos insulation around the hot pot with, e.g., fiberglass, and simultaneous provision of a removable lid for the pot to facilitate clean-out.

6.4   Development of LAMAPP to Use Replacement Materials.

Similarly, the LAMAPP and developmental "cold" machines need to incorporate state-of-the-art technology. The content of Appendix J must be given full consideration in this effort. Details of a new program to accomplish this presently are being discussed by PAD and Research Directorate, CRDEC.

7.   CONCLUSIONS AND RECOMMENDATIONS.

7.1   Conclusions.

It is concluded that several materials have been identified that are viable candidates to replace DOP in Q127 and LAMAPP penetrometer machines. All of these materials are members of families of chemical compounds that are characterized by low toxicity.

Rankings of the candidate materials in order of probable success (most probable first) are given with technical and operating specifications in Table D-2. of Appendix D for the Q127 machine; similar data are given in Table E-1. in Appendix E for the LAMAPP machine.

Table 7 summarizes the rankings of materials for both the Q127 and LAMAPP machines, with sources of supply. Additional data for specific materials can be found in Tables 4 or 5. Note in Table 7 that some replacement materials can be used in both machines, although they are ranked differently. Thus, one material might become standardized for use in both machines, as was the case with DOP.

It is further concluded that the materials identified here as DOP alternatives or replacements are generally inexpensive, and readily available. Aging tests at elevated temperatures, which are presently underway, should identify any candidate materials that are thermally unstable. But most candidates should prove to be at least as stable in long-term operation as is DOP. Indeed, some candidate materials that contain significant percentages of "impurities" (compounds similar to the primary compound, but more volatile) actually seem to improve in performance with aging at elevated temperatures.

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Table 7. Recommended Replacement Materials for DOP in the
Q127 and LAMAPP Machines, Ranked in Order of
Probable Success.

Rank -ing*	Q127 Machine		LAMAPP Machine	
	Chemical Name	Manufacturer or Source	Chemical Name	Manufacturer or Source
1	isostearic acid (76%) Emersol 875	Emery Div., Quantum Chem.	synthetic hydrocarbon Emery 3002	Emery Div., Quantum Chem.
2	isostearic acid (66%) Emersol 871	Emery Div., Quantum Chem.	isostearic acid (76%) Emersol 875	Emery Div., Quantum Chem.
3	synthetic hydrocarbon Emery 3004	Emery Div., Quantum Chem.	methyl oleate stearate Emery 2219	Emery Div., Quantum Chem.
4	synthetic hydrocarbon Emery 3006	Emery Div., Quantum Chem.	synthetic hydrocarbon Emery 3004	Emery Div., Quantum Chem.
5	oleic acid (71%) Industrene 206LP	Humko Chem. Div., Witco		
6	oleic acid (74%) Emersol 233LL	Emery Div., Quantum Chem.		

*   Highest rankings have highest probability of success.
** All are liquids at room temperature, assumed to be 20°C (68°F).

7.2   Recommendations.

Notification of the probable success of two candidate materials, isostearic acid and Emery 3004 synthetic hydrocarbon, was first given to PAD and to LANL in October, 1988, with the recommendation that testing and toxicological screening be initiated promptly as outlined in the ESP.

These two materials, and others summarized in Table 7, can be expected to perform well in "hot pot" machines including the Q127, and nearly as well in the "cold pot" LAMAPP machine where a less viscous, more volatile synthetic hydrocarbon (Emery 3002) probably would outperform Emery 3004 (see Table 7).

It is recommended that PAD and other agencies systematically pursue operational and toxicological investigations of candidate materials recommended and prioritized here until such time that one or more of these materials is approved for use in scenarios where human respiration of their aerosols is possible. "Hot pot" machine applications should be considered first, since the risk of thermal degradation of materials is greater here than in "cold pot" machines, and degradation products themselves might be toxic.

Over the longer term, it is recommended that improvements to Q127 and other "hot" machines in the field be considered as outlined in Section 6.3. here. Concurrently, the development of the LAMAPP system as a new-generation penetrometer is recommended, as discussed here in Section 6.4.

Finally, it is recommended that the replacement materials identi-fied here also be evaluated for use in "cold smoke" machines which use spray-generated aerosols having broad particle size distributions, and in which problems arise such as rancidity when corn oil is used. We believe that many of the materials identified in the present study would perform suitably in cold smoke applications.

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APPENDIX A

PROPERTIES AND ENVIRONMENTAL HAZARDS OF

DI (2-ETHYLHEXYL) PHTHALATE ("DOP")

FROM REFERENCE 1

IDENTIFIER	CHEMICAL NAME	CAS REG NO.
*DOP	Di (2-ethylhexyl) phthalate	117-81-7

CHEMICAL FORMULA: $C_6H_4 (COOCH_2CH(C_2H_5)(CH_2)_3CH_3)_2$

SYNONYMS: Bis (2-ethylhexyl) phthalate, di-sec-octyl phthalate; phthalic acid, bis (2-ethylhexyl) ester; di (2-ethylhexyl) orthophthalate; 1,2 benzenedicarboxylic acid (bis (2-ethylhexyl) ester).

DESCRIPTORS: DOP belongs to a class of compounds known as the phthalate esters, and is a diester of a benzene dicarboxylic acid.

*The identifier "DOP" is used to refer to both dioctyl phthalate and di-2-ethylhexyl phthalate. In this data package, the identifier "DOP" will refer to di-2-ethylhexyl phthalate.

CHEMICAL AND PHYSICAL PROPERTIES: DOP is a colorless, oily, stable liquid which is slightly soluble in water, but very soluble in organic solvents and mineral oil. Selected chemical and physical properties are listed below:

Property	Value (Ref)	Property	Value (Ref)
Molecular weight	391 (1)	Viscosity (centistokes)	80.0, 20°C (1)
Boiling point	384°C (2)	Vapor pressure Hg, 20°C (1)	7.10×10^{-8} mm
Melting point	-50°C (1)	Vapor specific gravity	13.5 (2)
Specific gravity	0.98, 25°C (1)	Volatility	1.32×10^{-3} mg/m^3 (1)
Flash point (open cup)	216°C (2)	Solubility (water)	< 0.01 g/100 ml (1)

MILITARY APPLICATION: Since DOP simulates agent aerosol behavior, the Army is currently using it to perform mask servicability tests and vehicle penetration/vulnerability tests.

INDUSTRIAL APPLICATION: DOP has been used as a plasticizer for resins and elastomers, and is found in floor tiles, various types of furnishings for households and transportation vehicles, food packaging systems, industrial tubing and conduits, medical tubing, catheters and blood containers, certain types of dental material, coatings for drugs, and numerous other products. The phthalate esters are also used as defoaming agents in manufacturing paper, as a vehicle for perfumes, in cosmetic products and in lubricating oils.[3]

ENVIRONMENTAL LAWS AND REGULATIONS: DOP is listed in the TSCA inventory.[4] In 49 CFR 173.115(b), DOT identifies the compound as a combustible liquid, while the hazardous materials' table in 49 CFR 172.101 gives its handling guidelines. Under the RCRA, the compound is listed as a hazardous waste (U028) in 40 CFR 261.33. Under the FWPCA, it is classified as an organic toxic pollutant (13B) in Appendix D of 40 CFR 122.53. The reportable quantity for this compound, under the CERCLA, is currently 1 pound, although under proposed CERCLA regulations, the reportable quantity will be raised to 5000 pounds (48 FR 23552; May 25, 1983). EPA's proposed water quality criteria for protecting human health from DOP's toxic properties range from 15 mg/l (for ingestion of water and contaminated aquatic organisms) to 50 mg/l (for ingestion of contaminated aquatic organisms alone) (45 FR No. 231, 79339, November 28, 1980).

ROUTE	SPECIES	DOSE	TOXIC EFFECTS (Reference)
Oral	Man	143 mg/kg	TD_{Lo} (4)
	Rat	31,000 mg/kg	LD_{50} (4)
	Rabbit	34,000 mg/kg	LD_{50} (4)
	Mouse	30,000 mg/kg	LD_{50} (4)
Skin	Guinea Pig	10,000 mg/kg	LD_{50} (4)
	Rabbit	25,000 mg/kg	LD_{50} (4)
	Rabbit	500 mg/24 hr	Mild irritation (4)
Inhalation	Mammal	30,000 mg/m^3	LC_{50} (4)
Eye	Rabbit	500 mg/24 hr	Mild irritation (4)
	Rabbit	5 mg	Severe irritation (4)

Mutagenicity: DOP is mutagenic to mice when administered intraperitoneally.[4,5]

Reproductive Effects: Singh et al.,[6] reported that the intraperitoneal injection of large doses of DOP (about one-fourth to one-eighth the LD_{50}) into rats on days 5, 10 and 15 of pregnancy caused teratogenic effects, which included resorptions, gross abnormalities, and skeletal abnormalities. When administered orally to rats and mice, DOP effects adult reproductive functions and developing embryos at TL_{Lo} values above 35 mg/kg (for rats) and 1000 mg/kg (for mice).[5]

Tumorigenicity: Administered orally, DOP is carcinogenic at doses above 216 gm/kg in rats and 260 gm/kg in mice.[4]

Ecotoxicity: EPA reported[4] the following aquatic toxicity values in support of proposed water quality criteria for the "phthalate esters":

Final EPA Value (in micrograms/liter)

Category	Fresh Water	Salt Water
Fish, acute	not available	not available
Invertebrate, acute	450	not available
Fish, chronic	0.63	not available
Invertebrate, chronic	less than 0.59	not available
Plant	not available	

(44 FR 43690, July 25, 1979)

Human Exposure Criteria: TLV-TWA 5 mg/m^3; TLV-STEL 10 mg/m$^{3(7)}$

OSHA Standard (air) TWA[3] 5 mg/m^3 (draft technical standard available)[4]

DOP's toxicity is extremely low by oral and dermal routes of exposure. This compound is poorly absorbed through the skin and no significant irritant response from dermal application or sensitizing potential has been noted in animals or humans.[4] DOP is approved by FDA as a plasticizer (21 CFR 175.300) and as a component of adhesives for use in the packaging, transporting, and holding of food (21 CFR 175.105).

CHEMICAL REACTIVITY:[9]

Azo Compounds: The aliphatic diazo compounds, especially diazo methane, are extremely reactive alkilating compounds and may react in some way to yield heat.

Caustics: The phthalate esters are easily hydrolyzed by caustics to a salt and alcohol with the generation of heat.

Explosives: The phthalate esters may form highly oxygenated compounds with metal nitrates that are more unstable than the original explosive. They may react exothermally with other compounds to cause explosive decomposition and yield extremely toxic fumes.

Mineral Acids: Strong mineral acids tend to cause hydrolysis and decomposition of the phthalate esters with the generation of heat.

Oxidizing Mineral Acids: The exhaustive oxidation of DOP can cause decomposition with the generation of heat. The conversion to phthalate acid and subsequent decarboxylation can also occur.

ENVIRONMENTAL FATE: DOP is a colorless, oily liquid with a high boiling point and a very low vapor pressure (1.2 mm Hg at $200^\circ C$); therefore, the compound would have little impact on the quality of air if introduced into the general environment. This compound is subject to chemical degradation by hydrolysis. Under alkaline conditions, the phthalate acid salt and 2-ethylhexyl alcohol are produced. In animal studies, 2-ethylhexyl alcohol is metabolized and the phthalic acid is excreted.[19] Both phthalic acid and DOP are subject to biodegradation. Aerobic degradation of the diester in fresh water hydrosoil, and decomposition of phthalic acid by soil microflora have been observed. Although the ester has very low water solubility, it experiences a number of biological effects. Bioconcentration has been demonstrated with aquatic plants (Elodea canadiensis), algae (Oedogonium), arthropoda (Daphnia magna), mollusca (Physa), insects (Culex pipiens quinquefasciatus), and fish (Gambusia affinis).[10] When DOP was subjected to static culture flask biodegradability tests, it was almost completely bio-oxidized at the end of 3 weeks.[11] The compound is considerably more resistant to biodegradation than dimethyl, diethyl, di-n-butyl, and butyl benzyl phthalates which experienced 100 percent loss after a week of incubation.

In an aquatic environment, indigenous microbial populations degrade phthalate esters via enzymatic hydrolysis. The reaction rate varies with factors such as temperature, pH, the presence of oxygen, the structure of the ester, and other factors.

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APPENDIX B

ARMY SURGEON GENERAL'S POSITION ON DOP

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CI 05 211915Z APR 86 PP   UUUU   1111830

CDR AMCCOM ROCK ISL IL //AMSMC-SG//

CDR LEAD CHAMBERSBURG PA //SDSLE-QAA//

CDR DCASMA BOSTON MA

COMDT USACMLSCH FT MCCLELLAN AL //ATZN-CM-NC//

CDR ANAD ANNISTON AL //SDSAN-DAS-CP/SDSAN-DAO-SD//

CDR UMDA HERMISTON OR //SDSTE-UA-CEA//

CDR RMA COMMERCE CITY CO //SMCRM-SF//

CDR PUDA PUEBLO CO //SDSTE-PUS-R//

CDR SHAD LATHROP CA //SDSSH-QQS//

CG MCLB ALBANY GA //874//

CG MCLB MCLB BARSTOW CA //B830//

CDR TEAD TOOELE UT //SDSTE-COP-TNG//

CDR CRDC APG MD //SMCCR-SPS-FH/AMSMC-QAD-PA(A)//

CDR DPG DUGWAY UT //STEDP-CI-TD//

CDR NAAP NEWPORT IN //SMCNE-SR//

CDR 267THCHEMCO JOHNSTON ISLAND //APCA-OP-NBC//

CDR 47TH ASG BURTONWOOD UK //AERUK-IA//

CDR 21STSPTCOM KAISERSLAUTERN GERMANY //AERLO-MM//

CDR LBDA LEXINGTON KY //SDSAN-LAC//

SMCCR-ESP   AMSMC-PCS-AE
AMSMC-AS   "MINIMIZE CONSIDERED"
AMSMC-SF

MAJ JAKUBOWSKI, AMSMC-SG, 25818   COORDINATION:
                                    SMCCR-ESP
                                    AMSMC-AS
                                    AMSMC-SF

  JOSEPH A. JAKUBOWSKI, MAJ, MS, COMMAND SURGEON

                                    UNCLAS

OE CE 211915Z APR 86 PP UUUU 1111830

CDR PBA PINE BLUFF AR //SMCPB-QA//

CDR RRAD TEXARKANA TX //SDSRR-QA//

CDR 200TH TAMMC ZWEIRBRUECKEN GERMANY//AEAGD-MMC-RA-CS//

CDR 59THORDBDE PIRMASENS GERMANY //AEUSA-CB//

ZEN CDR 330TH ORD CO APO NY 09189//

ZEN CDR GENERAL SUPPORT CENTER AERAS-B-Q APO NY 09132//

ZEN GENTEX CORP/ WESTERN OPERATION 2824/ METROPOLITAN PLACE

PANAMA CA 91767//

ZEN INDUSTRIAL DESIGN LABS/ 12120 WAGNER STREET/ CULVER CITY

CA 90230//

ZEN WAREHOUSE SERVICE AGENCY/ GENERAL SERVICE CENTER//

CARL PASTARET/ APO NY 09132//

ZEN MINE SAFETY APPLIANCE CO/ PO BOX 428/ PITTSBURGH PA

15230//

ZEN SCOTT AVIATION/ 1900 WALKER AVENUE/ MONROVIA CA 91016//

ZEN ILC DOVER DOVER DE //

ZEN COMPUTER SCIENCE CORP SHREVEPORT LA //

INFO CDR WESTCOM FT SHAFTER HI //APCA-JAC/HARPER//

CDR CRDC APG MD //SMCCR-HV/SMCCR-CO//

03 05 211915Z APR 86 PP   UUUU   1111830

CDR AMC ALEX VA //AMCSG/AMCCN//

HQDA WASHDC //DASG-PSP/DAMO-NC//

CDR USADESCOM CHAMBERSBURG PA

CDR USAMC SURETY FIELD ACTIVITY DOVER NJ //AMXSA//

UNCLAS

SUBJ: DIOCTYLPHTHLATE {DOP} HEALTH ADVISORY {S: 12 MAY 86}

A. 3D END, HQDA, DASG-PSP, 12 FEB 86, TO LETTER, PINE BLUFF ARSENAL,

SMCPB-2A, 23 AUG 85, SUBJ: DIOCTYLPHTHLATE {DOP} IS/IS NOT A

POTENTIAL CARCINOGEN.

1. THE ARMY SURGEON GENERAL HAS TAKEN THE POSITION THAT DOP IS TO

BE CONSIDERED A SUSPECT CARCINOGEN.

2. M-14 DOP TESTER AND TDA-104 TESTER AND ALL OTHER DOP TESTER

USERS SHOULD TAKE APPROPRIATE ACTION TO PROTECT WORKERS OCCUPATION-

ALLY EXPOSED TO DOP AEROSOLS AND LIQUID.

3. APPROPRIATE ACTION SHOULD INCLUDE PROVIDING SPECIFIC MEDICAL

SURVEILLANCE, THE USE OF APPROVED PERSONAL PROTECTIVE EQUIPMENT IF

WARRANTED, INCORPORATION OF ENGINEERING CONTROLS TO REDUCE EXPOSURE

TO OPERATORS, AND PROVIDING INDUSTRIAL HYGIENE ASSESSMENT OF THE

EXPOSURES. IN ADDITION, WORKERS SHOULD BE FORMALLY ADVISED OF THE

04   05   211915Z APR 86 PP   UUUU   1111830

RISKS ASSOCIATED WITH WORKING WITH DOP.   ALL IMMEDIATE DOP USE AREAS

SHOULD BE LABELLED AS A "CANCER SUSPECT AGENT AREA", AND ACCESS

SHOULD BE LIMITED TO ONLY AUTHORIZED PERSONNEL.   THESE AREAS CAN

BE DEFINED AS AREAS THAT MAY OVEREXPOSE WORKERS TO DOP CONCENTRATION.

4. CONVERTING FROM DOP TO REFINED CORN OIL IS UNDER CONSIDERATION

TO FURTHER PROVIDE PROTECTION.   ONCE THIS IS ACCOMPLISHED, CONTROLS

DESIGNED TO REDUCE DOP EXPOSURES WILL BE RELAXED APPROPRIATELY.

5. LOCAL MEDICAL AND SAFETY STAFF ACTIVITIES SHOULD BE CONTACTED TO

MADE ACTUAL ASSESSMENTS OF DOP EXPOSURES AND CONSULTED FOR MORE

SPECIFIC INFORMATION.

6. AMCCOM ORGANIZATIONS USING M-14, TDA-104 AND ALL OTHER DOP

TESTERS ARE REQUIRED TO PROVIDE THIS HEADQUARTERS WITH THE FOLLOWING

INFORMATION IF DOP IS USED:

   A.   NUMBER OF WORKERS OCCUPATIONALLY EXPOSED TO DOP.

   B.   TYPE OF PERSONAL PROTECTION USED (E.G., TYPE OF RESPIRATOR,

GLOVES, APRONS, ETC).

   C.   CONFIRMATION OF LABELLING OF DOP USE AREAS AS "CANCER

SUSPECT AGENT AREAS."

   D.   USE OF LOCAL EXHAUST VENTILATION DESIGNED TO REDUCE

EXPOSURE TO DOP.

E. RESULTS OF BREATHING ZONE SAMPLES FROM LAST PERIOD TESTED.

F. CONFIRMATION AS TO WHETHER WORKERS ARE BEING SEEN BY A
PHYSICIAN FOR ROUTINE MEDICAL SURVEILLANCE THAT IS SPECIFIC FOR DOP
EXPOSURES.

G. PLANS TO PROVIDE WORKER EDUCATION WITH MILESTONES OR REPORT
OF LAST CLASS.

IF NO ACTION HAS PREVIOUSLY BEEN TAKEN IN ANY OF THE ABOVE AREAS,
THEN SO STATE. NEW INITIATIVES MUST BE REPORTED WITH MILESTONES
FOR COMPLETION. M-14, TDA-104 AND ALL OTHER DOP TESTER USERS MUST
CONFIRM THAT DOP IS STILL BEING USED.

7. PROVIDE THIS INFORMATION TO HQ, AMCCOM, ATTN: AMSMC-SG, ROCK
ISLAND, IL 61299 NLT 12 MAY 1986.

8. POC IS MAJ JAKUBOWSKI, AV 793-5818.

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APPENDIX C

APPROVED TEST PLAN:

"ALTERNATIVE FOR DOP "

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TEST PLAN: "ALTERNATIVE FOR DOP"

Reference: Engineering Study proposal (ESP F1-7-8860 (Revised 11 Aug 87)

1. BACKGROUND

The referenced ESP requires that Research Directorate (RD) submit a detailed Test Plan outlining their effort to find an alternative for DOP (also called DEHP) in filter penetrometer testing. A kickoff meeting was held 19 Oct 87 at which Mr. Larry Friedman (PAD), Project Engineer (PE), and Mr. Hugh R. Carlon (CRDEC, RD), Principal Investigator (PI), agreed to the effort and scheduling which are detailed below.

2. STATEMENT OF WORK:

In this effort Research Directorate (RD) will attempt to identify an alternative material for DOP that (1) has acceptable toxicological properties, (2) performs acceptably in filter penetrometer systems, and (3) has other attributes such as reasonable cost. Ideally, an acceptable material already cleared by the Surgeon General might be identified. Otherwise candidate materials must be screened and, if an alternative for DOP is identified, action to have it cleared for use will be initiated. The scope of the present work does not permit toxicological testing of candidate materials to be performed. Thus, the approach must be to study candidate materials that are least likely to be toxic based on presently-available information, and to contemplate toxicological scrutiny only of a promising alternative for DOP, should one be identified, in subsequent work.

Research Directorate's (RD's) effort will include the following:

a. Investigate prior research studies, reports and papers.

b. Identify alternatives for DOP/DEHP, beginning with materials that have been cleared by the Surgeon General and have appropriate physical properties. If no such materials can be found, then candidate materials will be selected which have appropriate physical properties. Some candidate materials include tetraethylene glycol (TEG), pentaethylene glycol (PTAEG), hexaethylene glycol (HEXEG), oleic acid, di-(2-ethylhexyl) sebacate (DOS/DEHS), erythritol, pentaerythritol, and glyceryl monostearate (a wax). Corn oil will not be evaluated. RD shall procure promising materials having appropriate physical and promising toxicological properties. Candidate materials should be non-carcinogenic, nomutagenic and nontaratogenic, since they must eventually meet approval by the Surgeon General. No materials that have been disapproved by the Surgeon General will be considered.

c. Examine physical properties, chemical properties, toxicological properties, materials commercial availability, and material unit cost. Prioritize, candidate materials from "most likely to succeed" to "least likely to succeed."

d. Other factors which must be considered in choosing a material to replace DOP/DEHP are:

(1) Maintenance. It is undesirable to use a material that will clog the tester and/or support fungus growth in same.

(2) Destructive vs. Non-Destructive Testing. DOP/DEHP penetration testing is considered non-destructive. The new material must also be non-destructive. In this context, "non-destructive" means not damaging to filters in standard test aerosol concentrations. This does not rule out the possibility that acceptable materials, and DOP/DEHP, might actually damage filters in massive concentrations.

(3) The new material shall be examined for and exhibit adequate stability and aging characteristics.

e. Submit prioritized list or promising candidate materials which have not been previously cleared by the Surgeon General to PAD for review by the Health and Veterinary Services Office for official approval/recommendations.

f. (1) Initiate testing with the Los Alamos Monodispersed Aerosol Prototype Penetrometer (LAMAPP) system, as agreed with Mr. Friedman (PAD), in the reasonable expectation that data gathered for DOP/DEHP and candidate replacement materials using the LAMAPP will be applicable as well to the old Q127 penetrometer system, and other systems presently using DOP/DEHP. This effort will be coordinated by the PI with Mr. Larry Ortiz at Los Alamos National Laboratory (LANL). The approach will be first to study DOP/DEHP in detail. The LAMAPP will be operated over a wide range of adjustments of flow rate and other parameters to observe effects upon aerosol geometric mean diameter (GMD) and geometric standard deviation (GSD). In this way, the ability to "tune" LAMAPP with candidate liquids to produce aerosols of $0.3\mu m$ GMD and <1.3 GSD in suitable mass concentrations will be assessed. Candidate materials will be prioritized as to ability to meet these specifications.

(2) Should the LAMAPP not be available for prolonged assessment of candidate materials as outlined in (1) above, testing will revert to an old Q127 system. An attempt will be made to use the PMS LAS-X Laser Aerosol Spectrometer to evaluate GMD and GSD in that case, since rapid monitoring of these is essential to the test schedule and is not reliably afforded by the "OWL" instrumentation provided with the old Q127 systems.

g. Based on these tests, recommend suitable material(s), if any, from which a stable "monodispersed" aerosol should be able to be generated by a Q127, or other existing, penetrometer system. Determine the optimum test parameters to achieve the stable "monodispersed" aerosol.

h. Advise PAD in performance of comparative testing between the new material(s) and DOP/DEHP on actual canisters as outlined in paragraph C.1.c.(8) of the ESP.

3. REPORTING:

Brief monthly leter reports shall be submitted to the PE beginning 30
Oct 87. A Final report shall be submitted to the PE within 90 days of
completion of work, and upon approval shall be published as a CRDEC
Technical Report (TR) or Special Publication (SP).

4. SCHEDULING:

As agreed by the PE and PI at the kickoff meeting the schedule
(milestones) in paragraph C.4 of the ESP is/are not acceptable because too
little time is allowed for meaningful performance of Phase I by RD as
compared to that for Phase II by PAD. Instead, the following schedule is
specified:

SCHEDULE

Milestone	Date Completed
Funds received by RD	30 Oct 87 (approx)
Candidate material delivered for Phase II testing	30 Jun 88
Continuing evaluation of candidate materials and advising PAD in Phase II testing	31 Jan 89
Delivery of Final Report to PE	30 Apr 89

(signed)

HUGH R. CARLON
Principal Investigator
Operational Sciences Branch
Physics Division
Research Directorate

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APPENDIX D

THE Q127 PENETROMETER MACHINE

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THE Q127 PENETROMETER MACHINE.

The Q127 (Figure D.1.) is one of at least three aerosol penetrometer machines that have been standardized by PAD and other organizations to perform testing with essentially monodispersed aerosols having a mean droplet diameter of 0.3μm. Other standard machine models are the Q76 and the Q107 aerosol penetrometers.

The Q127 machine can produce test flows of up to about 100 lpm (3.5 cfm), and is adjustable to test flows of 16, 32, 42.5 and 85 lpm. The Q76 machine can produce essentially monodispersed aerosols at test flows of 700 to 7000 lpm (25 to 250 cfm), and the Q107 machine can produce test flows of 0 to 70,000 lpm (0 to 2500 cfm). The aerosol concentration produced by all three machines is approximately 80 $\pm$ 20 mg/m^3.

The Q127 machine is used to test aerosol penetration through respirator canister filters, and is fitted with a semi-automatic test chuck for this purpose. The Q76 and Q107 machines are used to test larger, open-faced filters and filter banks.

All three machines presently are manufactured by Air Techniques, Inc. (ATI), 1716 Whitehead Road, Baltimore, Maryland 21207, telephone (301)-944-6037. ATI designates the Q127 machine as its Model TDA-100, the Q76 machine as its Model TDA-110, and the Q107 machine as its Model TDA-120. Since all three machines operate using the same principles including generation of a 0.3μm test aerosol at concen ations of up to 100 mg/m^3, it is reasonable that results obtained in the present work using our Q127 machine can also be reproduced in the larger Q76 and Q107 machines.

The discussion beyond this point will concern itself only with the Q127 machine; specifications for this machine (ATI Model TDA-100) are given on the two pages following Figure D.1. The present purchase price of a new, basic Q127 machine is $24,820.00, effective 1 April 1983.

The Q127 machine used by the authors in the research reported here was not a new machine like that shown in Figure D.1., but it was very similar in general appearance. Our machine was modernized to incorporate a digital temperature controller for the DOP/candidate "pot", and other features, by Mr. Frank Blaha of Experimental Fabrication Division, RD&E Support Directorate, CRDEC.

All Q127 machines provide several adjustments that allow the operator to control the test aerosol produced so that it has suitable characteristics including geometric mean diameter (GMD), geometric standard deviation (σ_g), and mass concentration. These adjustments are summarized in Table D.1., where their effects on GMD and σ_g are shown.
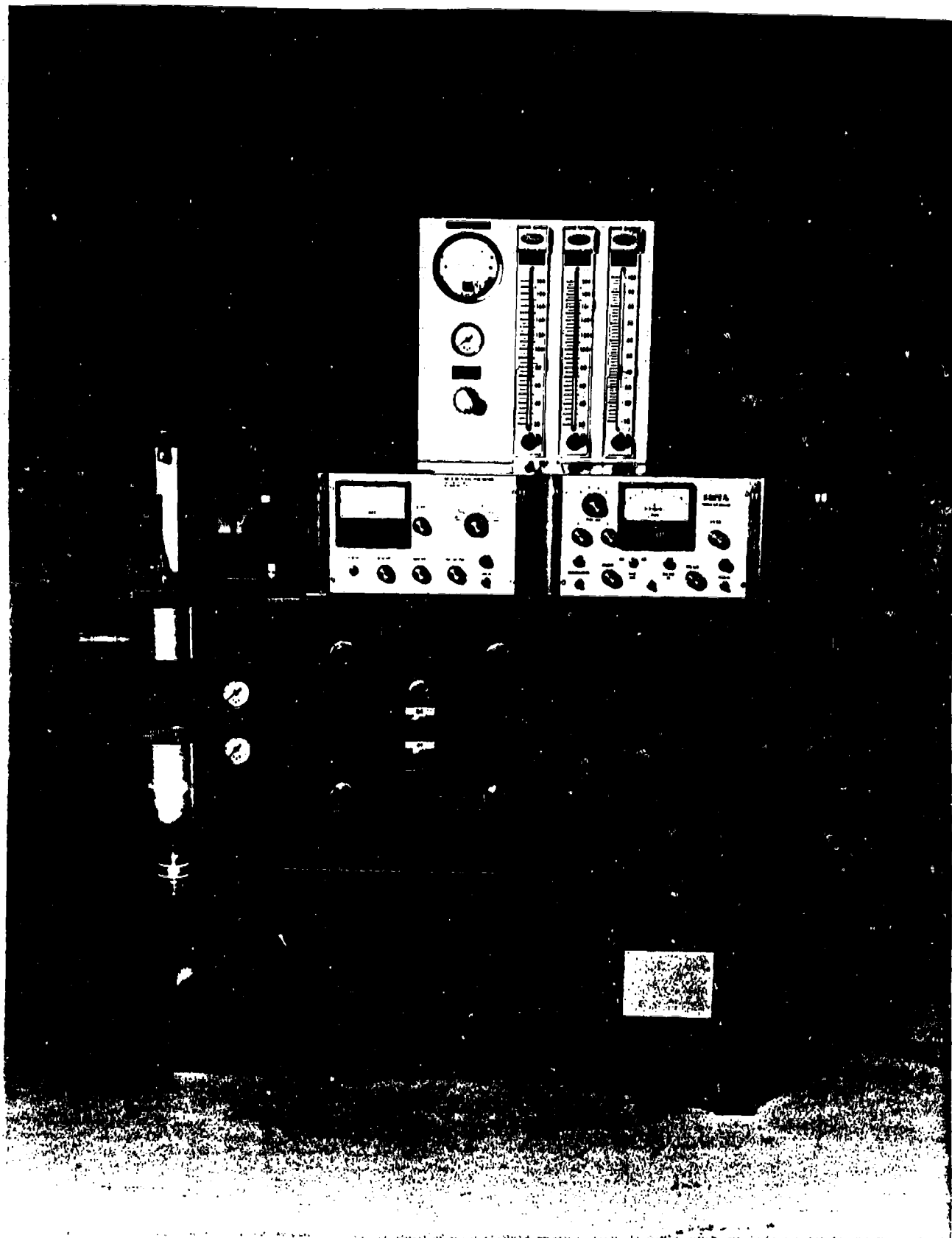
Figure D.1   The Q127 Penetrometer Machine (ATI Model TDA-100).

Table D.1   Effect of Q127 Machine Adjustments Upon Aerosol Produced.

Operator Adjustment	Effect on Geometric Mean Diameter (GMD)	Effect on Geometric Standard Deviation (GSD, σ_g)
Increase reservoir ("pot") temperature without changing other settings.	decreases	decreases
Increase quench air temperature.	increases	increases
Increase ratio of quench air to vapor pickup air.	decreases	decreases

Several candidate materials were identified in our research that performed suitably as DOP replacements. These are ranked according to probability of success (most probable first) in Table D.2., where operator adjustments needed to obtain the aerosol specifications shown also are indicated. With this information, the operator of another Q127 machine, old or new, should be able to duplicate our test results within the limits of statistical variation between machines.

Operators of machines other than the Q127, such as Q76 and Q107 machines, also should be able to duplicate our results as shown in Table D.2. by taking into account the normal range of adjustments used for operation with DOP and comparing individual settings with those in the table here.

TDA®-100 (Q127)
Monodispersed Aerosol Penetrometer

The TDA-100 Monodispersed Aerosol Penetrometer (Q127) incorporates the most advanced technology of unique design to make .3 micrometer monodispersed aerosol, measure and control the aerosol particle size and concentration plus measure the percent penetration of the tested component by the aerosol.

The TDA-100 is a basic apparatus consisting of three major components. They are:

1. The penetrometer itself consisting of the aerosol making and controlling equipment.
2. The particle size indicator and the mechanical analyzer which monitor the aerosol particle size.
3. The percent penetration indicator and associated light scattering chamber which measures the percent of aerosol penetrating the component being tested.

There are many adaptations and possibilities for various chuck and test fixtures which enable testing of a great variety of samples ranging from flat material to highly complex respirators.

In general the TDA-100 operates as follows:

Compressed air, passing through a filter and moisture trap, is connected to the penetrometer and regulated to a pressure of 35 pounds per square inch gage (psig). The air is then divided into two streams, vapor and diluent. The vapor stream flows at 20 liters per minute through a preheater, then into an aerosol generator and over the surface of liquid which is maintained at 165 ± 2°C. The diluent stream is cooled by a vortex tube and then heated by an electrical element. It bypasses the aerosol generator at a flow rate of 80 liters per minute and joins the vapor stream on the outlet side of the generator to make an aerosol. The aerosol is passed into an aging

chamber where it is stabilized. During testing, aerosol flows from the aging chamber to the chuck or test fixture adaptation and through the component under test. As aerosol is continually being made when the penetrometer is operating and testing is intermittent, the excess aerosol is exhausted to the atmosphere from the aging chamber.

The aerosol particle size is maintained at a predetermined level by controls on the penetrometer and is monitored by the aerosol particle size indicator. This indicator electronically measures aerosol particle size from a sample of the aerosol continually passing through a mechanical analyzer. This

mechanical analyzer measures aerosol particle size by the degree of polarization of a light beam which passes through a sample of the aerosol. The particle size of the aerosol is controlled by adjusting the temperature of the diluent air stream.

A sample under test is subject to a concentration of aerosol of approximately 100 micrograms per liter. Using this concentration as a base line of 100%, the amount of aerosol penetrating the sample under test is measured by the percent penetration indicator. Such measurements are registered linearly on the meter.
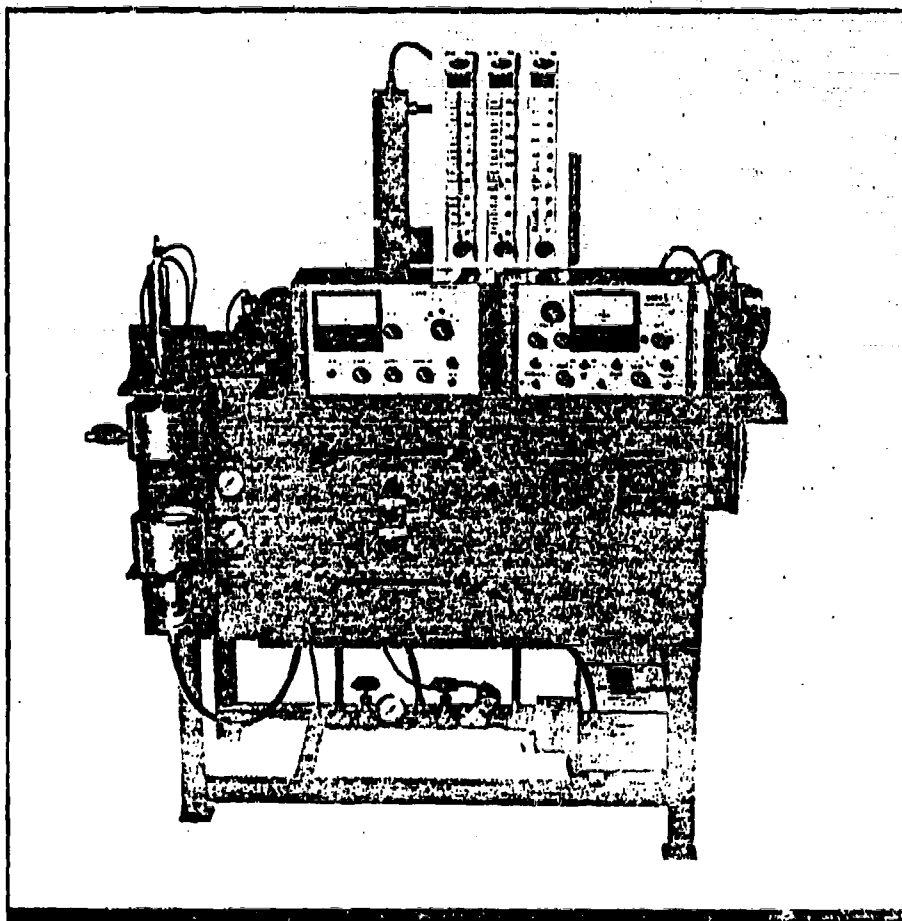
TDA®-100 Monodispersed Aerosol Penetrometer (Q127)

▬▬ MAJOR COMPONENTS AND SPECIFICATIONS

■ **AEROSOL GENERATOR:** Produces 0.3 micron aerosol at a concentration of 100 micrograms/liter

■ **VAPOR FLOWMETER:** Ranges from 5-50 SLPM @ 35 PSIG

■ **DILUENT FLOWMETER:** Ranges from 10-100 SLPM @ 35 PSIG

■ **TEST FLOWMETER:** Ranges from 16-85 SLPM @ 5" HG

■ **RESISTANCE INDICATOR:** Optional

■ **MECHANICAL ANALYZER:** Measures light-angle refraction from 0°-50° with four polaroid and three condensing lenses

■ **PARTICLE SIZE INDICATOR:** Solid state type, capable sensitivity of ten divisions to 1° rotation of Mechanical Analyzer, approximate size — 14" × 8" × 8"

■ **SCATTERING CHAMBER:** Forward light scattering, approximately 5" × 5" × 20" in size, with no dimming control and filter factor

■ **PERCENT PENETRATION METER:** Solid state type with ranges of 100%, 10%, 1% .1%, .01%. Approximate size — 14" × 8" × 8". Three place digital read out optional

■ **VORTEX TUBE:** 5 cubic feet per min. capacity

■ **MIXING CHAMBER:** Containing baffles with ports for exhaust, sample, inlet and test sample

■ **VACUUM PUMP:** Capable of delivering up to 85 SLPM @ 5"HG pneumatic, silent operating type

■ **AIR OPERATED CHUCK:** Manufactured to house customers' canisters of varying sizes, etc., to be tested

■ **CONSTANT VOLTAGE REGULATOR:** 250 VA rating. Input of 95-130 VAC output of 118 VAC ± 0.5%

■ **CONTROL PANEL:** Consisting of master "ON-OFF" particle size control, solid state time proportioning liquid temperature control, chuck control switches

▬▬ APPLICABLE STANDARDS AND SPECIFICATIONS

U.S. Federal Standard 209b, paragraph 50.
American Association of Contamination Control standards CS-1T, CS-2T and CS-6T.
American National Standards Institute N101.1-1972.
ANSI/ASME N510-1980.
Institute of Environmental Sciences IES-RP-CC-002-86.
American Society of Testing and Materials D-1899.
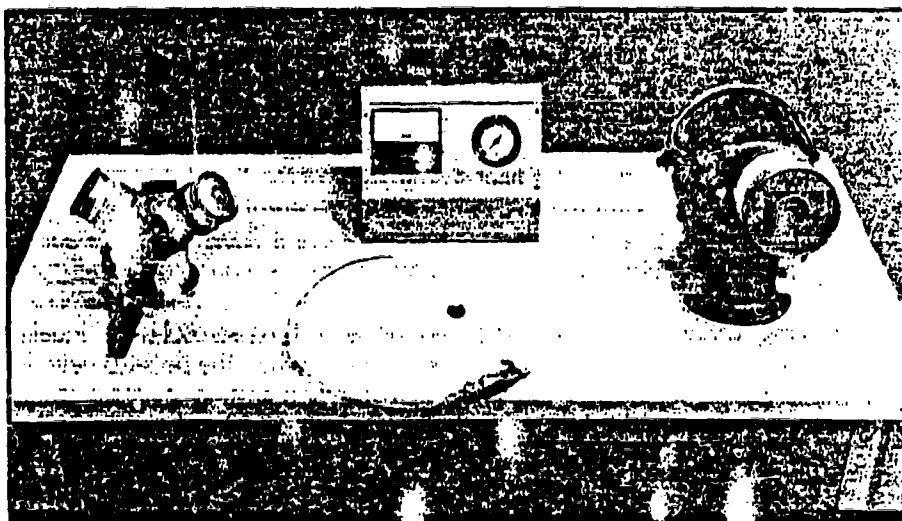
A test bench, TDA 101, is available as an accessory to the TDA-100 for testing leaks in facepieces of both full and half mask respirators. The bench has two test heads, a spray nozzle for aerosol, a penetration readout meter, valves, connectors and hardware for hook-up to the TDA-100 Monodispersed Aerosol Penetrometer.

ATI AIR TECHNIQUES INCORPORATED
1801 WHITEHEAD ROAD
BALTIMORE, MARYLAND 21207
TELEPHONE (301) 944-6037

Table D.2   Q127 Machine Settings to Achieve DOP Replacement Aerosols,
Showing Candidate Materials Ranked in Order of Probable Success.*

Rank -ing*	Material Trade Name	Typical Performance Range of CMD (μm)	Yield mg/m³	σg	"Owl" Readings for Range of CMD (degrees)	"Pot" Temp. °C	Part.Size Control (Voltage)	Ratio Quench/ Vapor Air	** Foot- notes
1	Eastman "eicosane"	.21- .30	87 87	1.25- 1.19	44, 46	170 170	0 0	90/10 90/10	1pm A.
2	Emersol 875	.20- .30	76 76	1.20- 1.25	35, 50	155 153	69 75	90/10 90/10	B.
3	Emersol 871	.20- .30	85 85	1.20- 1.22	36, 50	155 155	64 70	90/10 90/10	C.
4	Emery 3004	.20- .30	70 100	1.23 1.23	43, 50	170 180	46 75	90/10 90/10	D.
5	Emery 3006	.19- .21	110 110	1.20 1.20	35, 35	195 195	87 87	90/10 90/10	E.
6	Industrene 206LP	.18- .30	200 66	1.29- 1.31	34, 49	170 160	79 75	90/10 90/10	F.
7	Emersol 233LL	.19- .30	76 76	1.25- 1.40+	35 at 0.20 CMD	160 160	72 82	90/10 90/10	G.
8	Kemester 105	.26- .32	698 698	1.38 1.38	48, 48	166 166	0 0	90/10 90/10	H.
FOR COMPARISON: DOP		.19- .20 .25	146 146 146 146	1.21- 1.22 1.30- 1.54	29, 29 48, 48	172 172 172 172	38 38 100 100	80/20 80/20 80/20 80/20	I.

Test Conditions: a.   Quench air held at 25°C before heating.
                    b.   Line vacuum 5 in. water.
                    c.   Air flow rates: through test chuck 32 lpm; through Owl 5 lpm.

*   Highest rankings have highest probability of success; materials not listed
are not considered to be viable candidates for the Q127 machine.

**   (continued next page)

Table D.2 (concluded)

** Footnotes:

A. Impure sample; no longer commercially available (see text).

B. Isostearic acid, Emery Div., Quantum Chem. Co., 70-76% pure; **also performs well in the LAMAPP machine**.

C. Isostearic acid, Emery Div., Quantum Chem. Co., 60-66% pure.

D. Synthetic hydrocarbon, 85%, Emery Div., Quantum Chem. Co.

E. Synthetic hydrocarbon, Emery Div., Quantum Chem. Co., strong odor- high "pot" temperature; 0.21 was max. CMD.

F. Oleic acid, 71%, Humko Chem. Div., Witco Corp.

G. Oleic acid, 74%, Emery Div., Quantum Chem. Co.

H. Methyl oleate, 69%, Humko Div., Witco Corp.

I. The "standard" for candidate performance (see Sec. 4.4).

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APPENDIX E

THE "LAMAPP"

PROTOTYPE PENETROMETER MACHINE

WITH "LAS-X" AEROSOL SPECTROMETER

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THE "LAMAPP"

PROTOTYPE PENETROMETER MACHINE

WITH "LAS-X" AEROSOL SPECTROMETER

The Los Alamos Monodispersed Aerosol Prototype Penetrometer ("LAMAPP") was developed at the Los Alamos National Laboratory during a research program funded by the Product Assurance Directorate (PAD) of the U.S. Army Armament, Munitions and Chemical Command (AMCCOM). The purpose of the program was to design, build, and test a prototype respirator filter test penetrometer with improved performance over the aging Q127 test system (Appendix D). The improved penetrometer was to incorporate state-of-the-art principles, components, technology, and procedures for the task of testing respirator filters.

The specific design goals were:

- to produce from di-(2-ethylhexyl) phthalate (DEHP or "DOP", Appendix A), a stable test aerosol having a geometric mean diameter (GMD) of 0.3μm with a geometric standard deviation (σ_g) of 1.20 or less;.

- to provide a reliable means of monitoring the size, distribution, and concentration of the test aerosol;

- to produce a system capable of providing filter test flow rates of 16, 32, 42, 64, and 85 lpm;

- to provide rapid response filter penetration measurements to the 0.03% level.

Figure E.1. shows the cart-mounted LAMAPP system that was delivered to PAD and is now in side-by-side operation with a Q127 machine in the Research Directorate of the U.S. Army Chemical Research, Development and Engineering Center (CRDEC). The principle of operation is as follows.

In the LAMAPP, an evaporation/condensation type of aerosol generator is used to produce a nearly monodisperse aerosol for testing filters. The principle employed is to evaporate a liquid to a vapor, and then to condense this vapor onto salt (NaCl) nuclei to form small individual particles comprising the test aerosol or smoke..

Unlike most evaporation/condensation generation processes, the LAMAPP utilizes a polydisperse aerosol to initiate production of a final, nearly monodisperse aerosol. The fine polydisperse aerosol is first generated by room temperature nebulization (atomization) of an organic liquid like DOP, followed by flash evaporation. This procedure allows rapid vaporization of small particles at temperatures well below the primary liquid boiling point.
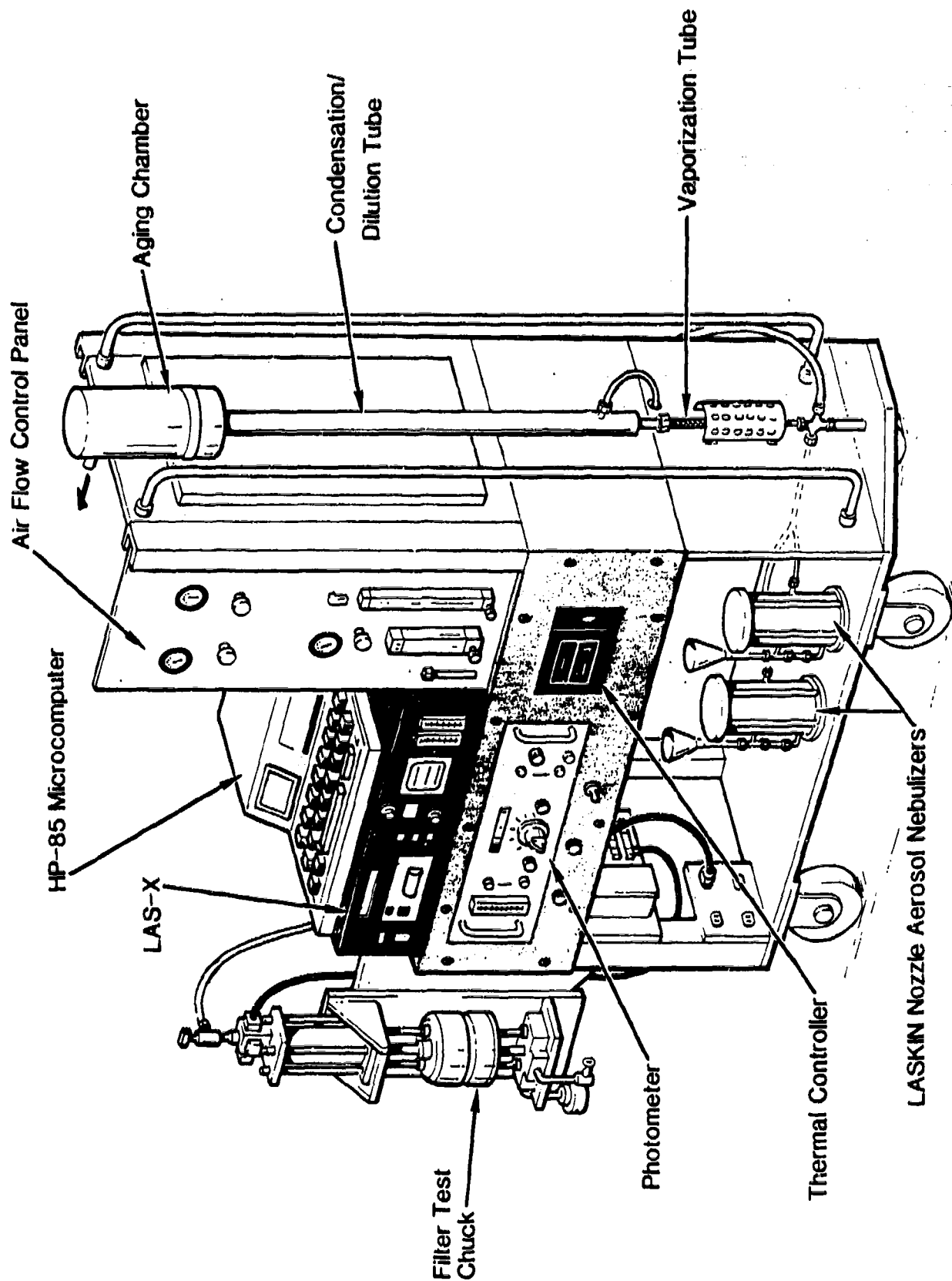
Figure E.1   "Monodisperse" Aerosol Penetrometer ("LAMAPP").

Thus, the vaporization temperature can be kept much lower than for the conventional method of boiling a liquid in a heated container, thereby decreasing any thermal decomposition.

In a separate nebulizer, an aerosol is generated simultaneously from a dilute NaCl solution and then is mixed into the liquid particle aerosol stream before both aerosols enter the vaporizer. The NaCl solution droplets dry to very small nuclei particles that do not evaporate because of the high vaporization temperature of salt.

The DOP or other organic vapor is condensed in a coaxial condensation tube that provides locally an unchanging environment for the rapidly-condensing vapors, while the NaCl aerosol provides excess nuclei to initiate and control condensing particle growth.

This unique condensation process is accomplished by injecting high concentrations of the hot, vaporized organic material at relatively high velocities (about 30 m/sec) into a slower-moving (about 5 m/sec) coaxially flowing, clean, cool air stream in the presence of the excess NaCl nuclei. Thus the geometry of the vapor injection and coaxial air cooling flow provide the rapid local mixing/cooling/dilution environment necessary for controlled condensation of individual particles from the organic liquid's vapor phase.

The condensed liquid aerosol has a nearly uniform particle size, and it is then delivered to the Filter Test Chuck system for filter tests. Filters are tested by comparing the concentration of the aerosol penetrating the filter to that challenging the filter. Both concentrations are determined by standard light scattering techniques, utilizing isokinetic sampling upstream or downstream of the filter being tested. From the ratio of the two concentrations, a fractional penetration and filter factor (FF) can be calculated.

The LAMAPP can produce mass aerosol concentrations of 25 mg/m^3 at flow rates of 100 lpm. Aerosol size distribution parameters (log-normal distribution) can be controlled closely and reproduced over the range from about 0.2 to 0.5µm GMD with a corresponding σ_g of 1.20 or less, using DOP as the organic liquid.

A brief description of the major subsystems and components of the LAMAPP is given in the following paragraphs. Refer to Figure E.1. for the general location of the components. Refer to Figure E.2. for a schematic diagram of the polystyrene latex (PSL) calibration subsystem, and to Figure E.3. for a schematic diagram of the air flow through the LAMAPP system.

The PSL calibration subsystem is used to calibrate the LAS-X Laser Aerosol Spectrometer (described on the following pages) before the LAS-X is used for aerosol size measurements. The small sampling tube from the LAS-X is inserted into a PSL supply tube on the LAMAPP panel during calibration.

A commercially available glass DeVilbiss nebulizer (Figure E.2.) is used to generate monodisperse PSL aerosol from standard or reference PSL water solutions. The solution stream is sheared by a high velocity
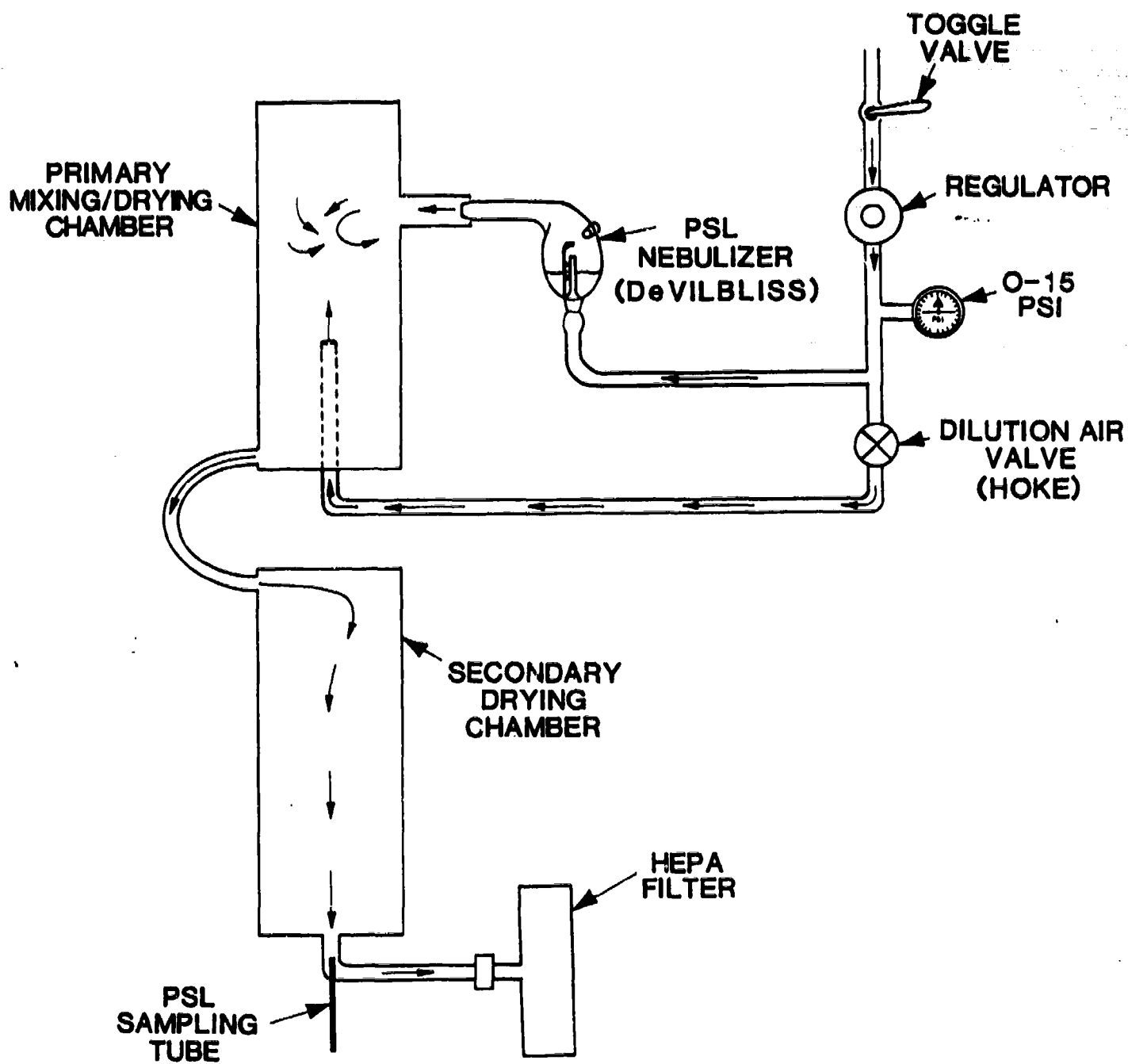
PSL CALIBRATION SUBSYSTEM

Figure E.2   Polystyrene Latex (PSL) Calibration Subsystem.

AIR FLOW DIAGRAM – PROTOTYPE PENETROMETER

Figure E.3   Air Flow Diagram for "LAMAPP".

airstream in the nebulizer to produce a sub-micron aerosol. Larger droplets leaving the nebulizer are impacted on its upper curved surface, and almost all droplets leaving the nebulizer contain only one PSL sphere; these evaporate to leave a nearly monodisperse aerosol of solid PSL spheres.

The Test Aerosol Subsystem provides nearly monodisperse aerosols of DOP or other organic liquids to the penetrometer. Its operation can be understood by reference to Figure E.3., where its components are shown at the bottom of the figure.

Compressed air is dried, cleaned, and regulated for delivery to the NaCl and DEHP (DOP) generators. The DEHP (DOP) generator, which may, of course, contain another candidate DOP replacement material, uses a Teflon Laskin nozzle to shear and entrain the liquid into airborne droplets. The size of the droplets decreases as the air pressure is increased. The resulting polydispersed liquid droplet aerosol is then evaporated in the Vaporization Tube (see Figure E.1.), which is wrapped with a heating tape (labeled "HEAT TAPE" in Figure E.3.).

The NaCl generator (Figure E.3., bottom) generates a solid aerosol of condensation nuclei from a 0.3% weight/volume NaCl water solution. This solution concentration must be used to obtain the target 0.3μm diameter aerosol of DOP or another material. The NaCl generator functions like the DOP or other liquid generator just described, using a Teflon Laskin nozzle in a Teflon "pot" at room temperature. The NaCl aerosol joins the DEHP/DOP or other aerosol prior to entering the Vaporization Tube (Figure E.3.).

The Vaporization Tube temperature is held at a constant temperature between 150°C and 160°C to vaporize the DEHP/DOP, or other liquid, aerosol. The NaCl solution aerosol is dried in the tube, but is otherwise unaffected by its passage. A Temperature Controller (Figure E.3.) controls the heating tape, and thus the tube temperature. The tube is stainless steel.

Any excess liquid falls into a trap at the bottom of the tube. Leaving the Vaporization Tube, the vaporized liquid and the NaCl condensation nuclei enter the Teflon Condensation/Dilution Tube (Figure E.1.), where the liquid's vapor recondenses onto the NaCl nuclei in a controlled manner to produce a nearly monodisperse aerosol. Clean air entering the vertical tube (Figure E.3.) also cools and dilutes the aerosol.

In the Aging Chamber (Figures E.1. and E.3.) the aerosol is mixed to a uniform concentration and the size distribution is stabilized. The aerosol then flows to the Filter Test Chuck, where test filter canisters are held and sealed semi-automatically using a manually-actuated pneumatically-operated drive system. Air at 30 psig closes and seals the chuck (Figure E.3.), which is equipped with safety features including the requirement for two-hand operation.

Leaving the Test Chuck, the aerosol stream splits and flows to a Photometer and also, through an aerosol Capillary Diluter, to the LAS-X

Laser Aerosol Spectrometer (Figures E.1. and E.3.). The LAS-X is described below, and also in the manufacturer's specification sheets on the following pages.

In the photometer, forward-scattered light produces an integrated signal for all particles greater than 0.1µm in diameter. Samples from upstream or downstream of the test filter are selected by switches on the Photometer front panel. The relative concentration of the aerosol sample before and after the test filter thus is established, giving the filter's protection factor. Absolute aerosol concentration is determined, when desired, by using a piece of filter paper in the chuck that is weighed before and after exposure to a known aerosol flow rate for a known time.

An HP-85 Microcomputer (Figure E.1.) calculates and prints aerosol size distribution data directly from data taken by the LAS-X spectrometer. Menus options are offered for sample repetition, data presentation and print out. Some example tapes are contained in Appendix I of the present report.

The LAS-X spectrometer sizes single particles at a rate of about $2000/cm^3$, transmitting particle size data to the HP-85 Microcomputer. During the year's measurements reported here, the LAS-X system had to be returned twice to the manufacturer for calibration, and was taken under a service contract following the second calibration as a precaution against downtime in the event of additional operating difficulties. See additional data on the two pages following Table E.1.

Of the many candidate DOP replacement liquids listed in Table 4 that were evaluated using the LAMAPP machine, several were found to work quite well. These are summarized in Table E.1. In this appendix, where LAMAPP machine settings necessary to achieve these results also are listed.

A comparison of Table E.1. with Table D.2. in Appendix D shows that some materials, including Emersol 875 (isostearic acid) and Emery 3004 (synthetic hydrocarbon), work quite well both in the LAMAPP and the Q127 machines. Thus, it might prove feasible to use one or more such liquid materials in both machines, just as it is possible to use DOP in this way.

Table E.1 **LAMAPP Machine** Settings to Achieve DOP Replacement Aerosols, Showing Candidate Materials Ranked in Order of Probable Success.*

Rank -ing*	Material Trade Name	Typical Performance Range of CMD (μm)	Yield mg/m^3	σ_g	NaCl Setting (psi)	Liquid Setting (psi)	Evap. Tube Temp., (°C)	Aerosol Dilution Air (lpm)	Foot- notes **
1	Emery 3002	.18- .28	23	1.18- 1.30	4.5 3.5	2.0 2.0	170 170	30 25	A.
2	Emersol 875	.195-.21	15	1.20	6.0	3.0	165	50	B.
3	Emery 2219	.21- .31	35	1.24- 1.20	4.3 3.6	2.0 2.0	135 135	40 50	
4	Emery 3004	.18-.23	26	1.32	5.0	3.0	165	35	C.
5	Emersol 233LL	.31	--	1.23	4.25	2.0	147	25	D.

FOR COMPARISON:

	DOP	.30	40-50	1.25	9.5	4.0	156	70	E.

Test Conditions: a. LAS-X air flows: sample 1 cm^3/sec; sheath 0.5 cm^3/sec.
  b. HP85 printing CMD graph and data table (Appendix I).
  c. System air flow: at test chuck, 32 lpm; pressure 15 psi.
  d. Sodium chloride (NaCl) solution 0.3% by weight in water.

* Highest rankings have highest probability of success; **materials not listed are not considered to be viable candidates for the LAMAPP machine**.

** Footnotes: A. Synthetic hydrocarbon, 99%, Emery Div., Quantum Chem. Co.
  B. Isostearic acid, Emery Div., Quantum Chem. Co., 70-76% pure, bypass air necessary at 1-3 lpm; **also performs well in the Q127 machine**.
  C. Synthetic hydrocarbon, 85%, Emery Div., Quantum Chem. Co., bypass air necessary at 5-7 lpm.
  D. Considered very promising, but not recommended for use in LAMAPP pending completion of future testing; bypass air necessary 3.0 lpm.
  E. DOP is the "standard" for candidate performance; see Sec. 4.4. Other CMDs have not yet been run with DOP in the LAMAPP machine pending SOP approval.

PARTICLE MEASURING SYSTEMS INC.

FEATURES
- Solid state photodetectors
- Long life He-Ne laser
- Greatest sensitivity — 0.09 μm
- 2.2π steradians collecting solid angle
- High resolution — 0.007μm
- Self-contained data system
- Sample intervalometer
- Self-contained printer
- PHA referenced to laser — AGC
- Low coincidence error
- Very low maintenance
- Serial RS232C output
- Built-in CRT Display
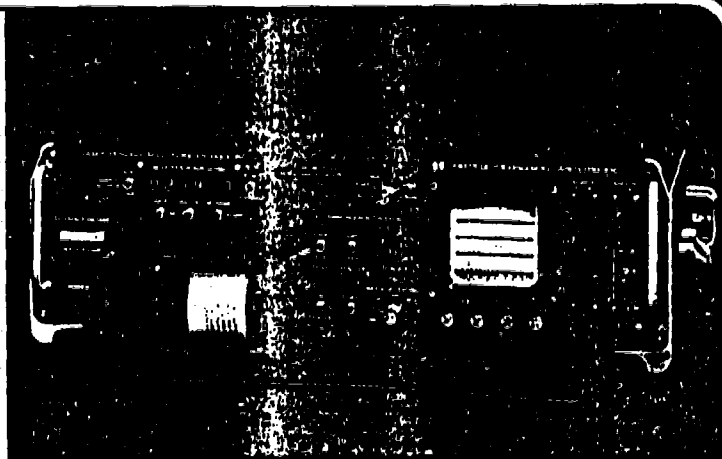
APPLICATIONS
- Clean room monitoring
- Filter testing
- Air pollution
- Smokes, dust, and fine powders
- Milling and chemical process controls
- Compressed gas monitoring
- Pharmaceutical manufacturing
- Mining
- Chemical and biological studies
- Engine exhaust particulate analysis

GENERAL DESCRIPTION

The standard LAS-X is offered with four overlapping size ranges with each size range divided into fifteen linear size intervals providing up to 60 size channels covering the 0.09-3.0 μm or 0.12-3.0 μm range. An additional size range of 0.12-7.5 μm is available. The LAS-X utilizes aluminum extrusions for mechanical stability. Laser and detector alignment are achieved with spring-loaded x-y screw adjustments. The LAS-X laser is a hybrid He-Ne 632.8 nm tube with an aluminum envelope specially designed for the LAS-X. The LAS-X pulse height analyzer (PHA) has its reference voltage derived from the source of illumination providing effective automatic gain control (AGC). Programmable amplifiers are used to gain switch and provide the size ranging to accommodate the large dynamic range of the instrument.

The method of particle sampling is with an aerodynamically focused jet which constrains particle flow to small diameter particle sample stream surrounded by a filtered sheath flow. The particle sample stream is positioned at the focus of a 5 mm parabolic mirror. The collected light is collimated by the parabolic mirror and after reflecting off a 45° flat mirror, it is refocused by an aspheric lens. A single photodiode detector with over 50% quantum efficiency converts the collected light into a signal photocurrent.

The LAS-X has an MOS memory with sixteen addresses. Fifteen of the addresses are used for particle size distribution storage. The remaining address is used for counting all particles larger than Channel 15. A selectable 6-digit decimal display is provided for real-time data monitoring requirements of precise particle counts. The LAS-X provides a built-in CRT for real-time displays of particle distribution functions. A line printer is built-in with automatic print functions. An asynchronous serial ASCII RS232C data output is standard.

OPTICAL SYSTEM

The LAS-X has a unique optical system with the largest collecting solid angle in the industry. The active laser cavity provides an energy density in excess of 500 W cm^{-2} with a beam width of 400-600 μm (0.09-3.0 μm range). The collecting optics include two front surface mirrors and an aspherical refracting element housed in a single aluminum block (optical/sample module).

The primary collecting mirror is a parabolic element of 5 mm f.l. which has been gold-plated to provide 90% reflectivity at 632.8 nm. Particles pass through its focus when in the sampling volume.

The second front surface mirror is dielectrically coated to provide better than 99% reflectivity at 632.8 nm. The dielectrically coated aspheric collecting lens completes the collecting optical system. The combined imaging system has an effective magnification of 4X. The system collects light from 35-120% providing a 2.2π steradian solid angle.

AIRFLOW SYSTEM

The airflow system in the LAS-X is a fully plumbed type with aerodynamic focusing. See Figure 2.

The sample flow enters the optical/sample module through an external intake. The shortest

PMS
DS-LAS-X
June 1982

Fig. 1. Optical System Diagram

Fig. 2. Air Flow Diagram

"OURS":
MODEL: LAS-X
4 RANGE — BUILT MARCH '85.
S/N 3768-0383
-119
PMS
BOB LUENK
(303)-443-7100

direct path is provided to the illuminated sample volume. The aerosol sample passes through a short section of hypodermic tubing (500 μm diameter) where it joins with a flow of filtered sheath air. The flow remains essentially laminar and is aerodynamically focussed by a nozzle. The aerosol sample stream is ~100 μm diameter when intersecting the laser beam.

The pump is a diaphragm pump having up to 6 liter min-¹ capacity. The sample flow and sheath flow can be independently monitored and set by the metering valves. 'O' ring seals are used throughout the optical/sample module. Connections are made with ⅛" pipe threaded fittings.

PERFORMANCE

The high resolution multiranging capabilities of the LAS-X have greatest importance in the submicron size range. Figure 3 illustrates the spectral resolution of the LAS-X with a mixture of three DOW latices on Range 2. The LAS-X is a full spectrometer with all size classes sampled simultaneously in the selected range. Size ranges may be manually selected; however, in the AUTO mode, the LAS-X will sequence through all size ranges. Size range and size channel information is encoded in the data outputs.

Fig. 3. Particle size spectrum from a mixture of 3 DOW latices showing resolution of LAS-X

SPECIFICATIONS

Size Ranges	Four ranges covering 0.09-3.00 μm Typically: 0.60-3.00, 0.24-0.64, 0.15-0.30, 0.09-0.195 μm
	Four ranges covering 0.12-3.00 μm Typically: 0.60-3.00, 0.24-0.64, 0.15-0.30, 0.12-0.20 μm
Number of Size Channels	16
Minimum Detectable Size	0.09 μm (0.09-3.00 μm) 0.12 μm (0.12-3.00 μm)
Size Resolution	0.007 μm typical (0.09-3.00 μm) 0.006 μm typical (0.12-3.00 μm)
Sample Flow Rate	0.5-1.5 cm³sec-¹ (0.09-3.00 μm) 1.0-10 cm³sec-¹ (0.12-3.00 μm) or (0.12-7.5 μm)
Maximum Number Density or Concentration for 90% Counting Accuracy @ 1 cm³ sec-1 Sampling Rate	17,000 cm⁻³ without coincidence dead time loss correction
Laser	He-Ne TEM₀₀ mode
Optics	Collecting optics consisting of a 6 mm f.l. parabolic mirror, a 45° plane mirror and an aspheric lens. Collected solid angle ~ 35-120° (>2π steradians)
Accumulator Capacity	16 channels with 20 million population per channel
Selectable Automatic Print and Reset Intervals	Selectable as: 1) 6 to 15 seconds in 1 second steps 2) 10 to 150 seconds in 10 second steps 3) 1 to 15 minutes in 1 minute steps 4) 10 to 150 minutes in 10 minute steps 5) 1 to 15 hours in 1 hour steps
Overload Print and Reset	An automatic print and reset is generated after any channel in the main accumulator exceeds 19 million
Printer Output	7-column printout on 2" thermal sensitive paper
	18 lines per print with time-of-day and total elapsed second plus 16 size channels.
Serial Output	Asynchronous serial ASCII RS 232C output. 6 ASCII decimal characters plus space per word. 18 words per frame with space replaced by line feed after 18th word.
Selectable Six-Digit Decimal Display	Selectable as: 1) Time-of-day in hours, minutes, seconds 2) Total elapsed seconds for current sample 3) Population of any channel in scope memory (normal, X10, or X100)
CRT Histogram Display	Bar graph display of size distribution on 4" CRT. Full scale vertical population selectable as 100, 1K, 10K, 100K, 1M, or 10M
Environmental	Temperature: 0 to +40°C Altitude: 0-20,000 ft (6.1 km) Humidity: 0-99% RH (noncondensing)
Power	115V, 50-60 Hz, less than 2 amps 100V, 220V, 240V, 50-60Hz optional
Dimensions	23 x 21 x 7 (58 x 53 x 18 cm)
Weight	Less than 60 lbs (18.2 kg)

APPENDIX F

Q127 MACHINE TESTING WITH PENTAETHYLENE GLYCOL

AND OTHER MATERIALS.

(REPRODUCED FROM REFERENCE 2)

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PROCEEDINGS of the

16th DOE NUCLEAR AIR CLEANING CONFERENCE

Held in San Diego, California
20-23 October 1980

Sponsors: U.S. Department of Energy
The Harvard Air Cleaning Laboratory

Editor
Melvin W. First

Published
February, 1981

ADDENDUM 1

SELECTED POLYETHYLENE GLYCOLS AS "DOP" SUBSTITUTES

B. V. Gerber
US Army ARRADCOM Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland

Abstract

The recommendation is made that Polyethylene glycol (PEG) 400 be considered as a substitute for "DOP" in aerosol generators producing a polydisperse distribution for testing the integrity of filters and filter assemblies and for testing respirator fit. Further, the recommendation is made that pentaethylene glycol (PTAEG) and possibly hexaethylene glycol be considered as a substitute for "DOP" in aerosol generators thermally producing "monodisperse" aerosol for quality acceptance tests according to US Federal specifications and standards. The toxicology data base available on the polyethylene glycol family of chemical compounds is discussed and the conclusion is drawn that the probability of approval and acceptance as a non-hazardous substance in the filter and filter media test role is high. Data and analysis supporting PTAEG performance equivalent to "DOP" in the filter and filter media test role are given or referenced. Cost and availability of the substitute materials is discussed. Conclusions based on the present data and information are given and recommendations for further work are made.

Objectives

The objectives of the effort herein described were (a) to conduct preliminary investigations and analyses of the use of certain polyethylene glycols as substitutes for di(2-ethylhexyl) phthalate (commonly known as "DOP") in both polydisperse aerosol generators and thermal ("monodisperse") aerosol generators as respectively used to determine the integrity of filters, filter assemblies, and respirator fit and the quality of filter media and filters, (b) to acquire and analyze information on the cost and availability of such substitute materials and (c) to acquire and analyze the available toxicology data base on these materials in order to assess the probability of approval and acceptance as non-hazardous materials in these testing roles.

Background

On October 15, 1980, the National Cancer Institute published a draft National Toxicology Program Technical Report[1] on di(2-ethylhexyl) phthalate, commonly known as "DOP". The report presents bioassay data on rats and mice and indicates that "DOP" causes increased incidence of hepatocellular carcinomas or neoplastic nodules in rats and hepatocellular carcinomas or adenomas in mice. Should the Secretary, US Department of Health and Human Services, or his designee, (OSHA), classify "DOP" as a Category I potential carcinogen, then the model standard set forth in CFR 1990.151[2] will apply. The standard will set the lowest feasible concentrations and time limits for inhalation, dermal and eye exposures to "DOP".

However, CFR 1990.151 also states in paragraph (c)(1)(i) that, when it is determined by the Secretary that there are available substitutes for all uses or classes of users that are less hazardous to humans, the proposal shall permit no occupational exposure. The determination of the acceptability of substitutes includes consideration of availability, practicability, relative degree of hazard and the economic consequences of the substitution. It is therefore to be expected that use of "DOP" would be precluded for any specific role for which a less hazardous substitute is shown to be available and where practicability and

economic feasibility can be demonstrated. The Secretary must conduct public hearings on the establishment of any standard which is then published in the Federal Register. In the case of "DOP", it is reasonable to expect establishment of a quantitative standard and/or the acceptance of substitutes for use in filter testing by the summer or fall of 1981.

The present report addresses the possibility that members of the class of chemical compounds known as polyethylene glycols can substitute for "DOP" in the various modes of filter, filter media and respirator testing.

Nature of the Polyethylene Glycols

The polyethylene glycol family has the following general formula:

$$HO(CH_2-CH_2-O)_nH$$
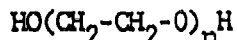
where: n = 1, 2, 3, 4, 5, ... defines a particular member of the family. The glycols are dihydroxy derivatives of the paraffins. Ethylene glycol (n = 1) is the simplest member of the family. Ethylene glycol may be considered to be intermediate between the mono-hydroxy compound, C_2H_5OH, ethyl alcohol, and the trihydroxy compound, glycerol, $C_3H_5(OH)_3$. As n increases, the members of the family change from liquids to waxy solids. The polyethylene glycols are prepared commercially by the condensation of ethylene oxide carried out in water or ethylene glycol made basic with sodium hydroxide. A mixture of polyethylene glycols results. In the United States, the major suppliers are the Union Carbide Corporation[3] and the Dow Chemical Company[4]. The polyethylene glycol mixtures are identified by their average molecular weight which is typically specified as 200, 300, 400, 600, 1000, etc. The polyethylene glycols are used in pharmaceutical preparations (ointments, lotions, suppositories, and tablet coatings) and cosmetics (lotions, creams. lipstick, cake make-up, etc.). Some are used as direct food additives (coatings, flavorings). There are many other industrial and chemical uses[3,4]. The human ingestion or exposure to the polyethylene glycols has led to considerable study of their effects on biological systems.

The polyethylene glycols are presently under consideration by the US Army for use in generating smoke in which to conduct troop training exercises.

Toxicology Data Base for Polyethylene Glycols

Table I is a summary checklist of available information on the toxicology data base of the polyethylene glycols. The information (with the exception of the current US Army studies) is available from the toxicology Information Response Center [5]. Other information sources are the literature of Union Carbide[3], Dow Chemical Company [4], and the Workplace Environmental Exposure Level Guide (Sept 1980) [6].

The US Army ARRADCOM Chemical Systems Laboratory (CSL) has been investigating the inhalation toxicity of Polyethylene Glycol 200 (PEG 200) for some time. The experimental phase of the studies is complete as of October 1980. All bioassay studies should be complete and a report written by the spring of 1981[7]. So far it appears that the material will be judged suitable for use as a safe training smoke to which unprotected humans can be exposed using relatively high concentrations.

Table I: Checklist Summary of Available Information,
Polyethylene Glycol Family

Type of Information	Routes Other Than Inhalation	Inhalation Route
Acute Toxicity[1]	Some available information	In process by US Army CSL
Subacute Toxicity[2]	Some available information	In process by US Army CSL
Subchronic Toxicity[3]	Some available information	In process by US Army-CSL
Chronic and Long-Term Toxicity[4]	Some available information	-
Human Tests[5]	Some available information	-

1. Acute Toxicity: Single exposure of up to 24 hours to a chemical by parenteral, oral, cutaneous, inhalation or other body routes of entry.

2. Subacute Toxicity: Any repeated exposure to a chemical for periods greater than 24 hours but usually within a time period of 21 to 30 days.

3. Subchronic Toxicity: Any repeated exposure to a chemical for periods greater than 30 days but usually for periods of 90 days or 13 weeks.

4. Chronic and Long-Term Toxicity: Chronic: Any repeated exposure to a chemical for periods greater than 90 days but usually for periods of 1 or 2 years, i.e., 52 or 104 weeks. Long-Term: Any repeated exposure to a chemical for periods greater than 104 weeks or for the lifespan of an animal species.

5. Human Tests: Any available information on human exposures.

Because of its intended use, the Army nominated polyethylene glycol (Chemical Abstract Services (CAS) Registry No. 25322-68-3) for carcinogenicity testing. On the basis of the available data however, the NCI Chemical Selection Working Group (CSWG) unanimously decided, in a meeting of June 28, 1979, that animal carcinogencity testing was not required for the polyethylene glycols[8]. The NCI evaluation of the data base was performed by Dr. E. Weisburger.

In summary of this section, it is evident that an extensive published toxicology data base exists for the polyethylene glycols as a class of compounds. This data base will shortly (spring 1981) include detailed quantitative information on animal exposure via inhalation. Some longer term animal carcinogenicity studies.

have been performed in the past but no information considered adverse was found as of 1978.

PEG Substitution in Polydisperse Aerosol Generators

"DOP" has been exclusively used to generate a polydisperse (relatively wide size distribution) aerosol for use in testing the integrity of clean rooms, clean benches, glove boxes, gas masks, HEPA filter banks and respirator fit.

At least two aerosol generation methods are in use. One method is based on the Laskin submerged nozzle as described by Echols and Young[9]. The liquid physical properties controlling the resultant particle size distribution are probably viscosity, surface tension and density. The liquid atomization process is very complex and dependent on nozzle geometry. A priori theoretical predictions for a particular nozzle cannot be made. Considering only liquid substitution and the same atomization system, a first approximation is that the average particle size will be related to the liquid properties through the Ohnesorge number, such that:

$$\bar{d} \propto \mu_L^2 / \rho_L \sigma_L$$

where:

$\bar{d}$ is the average drop size

μ_L is the liquid viscosity

ρ_L is the liquid density

σ_L is the liquid surface tension

All of the liquid polyethylene glycols have similar values for density (1.127) and surface tension (44.5). The Ohnesorge Number approximation therefore results in a selection based on essentially viscosity. Using this technique, PEG 400 (μ_L = 105) is the liquid which matches the Ohnesorge Number for "DOP". A sample of PEG 400 was sent to the Harvard Air Cleaning Laboratory for controlled quantitative comparison (particle size distribution) with other competitive candidate "DOP" substitutes in this generation mode. The preliminary results are reported by M. First in another paper in these proceedings (16th DOE Nuclear Air Cleaning Conference, San Diego, CA, Oct 1980). The preliminary results show that the count median diameter and the geometric standard deviation, as measured with an aerosol laser spectrometer[10] were in the acceptable range for a "DOP" substitute. It should be pointed out however that, if needed, adjustments of particle size could probably be made by blending with PEG 300 (for smaller size) or PEG 600 (for larger size).

The second mode of polydisperse generation consists of discharging a regulated quantity of liquid onto a heated area[11]. The liquid vapors are picked up by an inert carrier gas (nitrogen or argon) and condensed to a polydisperse aerosol. The liquid physical properties most important in this generation mode are probably vapor pressure and thermal stability. Corn oil, another candidate "DOP" substitute, decomposed in use but PEG 400 did not and is apparently an acceptable substitute[12]. (The flash point for PEG 400 by closed cup test is in excess of 350°F.)

The impact of the hygroscopicity of the polyethylene glycols on the stability and reproducibility of the test aerosol has been questioned[13]. Data are available[3] showing that, at equilibrium, the particle size because of water absorption

might increase 1% at 25% RH, 4% at 50% RH, and 11% at 75% RH. This factor does not appear to be significant but final determination should be made by extensive user test.

In summary to this section, PEG 400 (or a blend chosen for precise particle size distribution control) so far appears to be a good physical candidate as a "DOP" substitute in polydisperse aerosol generators. It is inexpensive and easily available and appears to reproduce the performance of "DOP" used presently in this aerosol generation mode. The extensive available toxicology data base, so far showing no adverse data, generates a high degree of confidence that this class of compounds will allow unprotected human exposure to reasonable and practicable concentration-time profiles.

Substitutes For Use in Thermal ("Monodisperse") Aerosol Generators

Standard Methods

High efficiency Particulate Air (HEPA) filters manufactured for the US Government are tested in accordance with the quality acceptance test procedures for filters and media contained in MIL Std. 282. The industry standard method for evaluation of air assay media is given in ASTM Std. D2986 and is essentially equivalent to the standard military test procedure for filter media.

In all cases, the standards require the generation of "DOP" test smoke by a thermal evaporation/condensation process. The design goal of the test generator is to produce a cloud of essentially monodisperse particles having a diameter of 0.3 μm and a mass concentration of 100 ± 5 μg/l. The particle size is monitored by an NRL particle size meter (owl)[14]. However, as shown by Hinds, First, et. al.[15], the NRL owl indicates an average size (weighted by the eighth power of diameter) if a distribution of particle sizes is introduced. Using a laser aerosol spectrometer, they showed that the Q-127 generator available to them could not achieve the design goal of ± 0.03 μm. In terms of the geometric standard deviation (GSD) they were able to achieve 1.15 but not the 1.1 desired. Arthur D. Little, Inc., under contract [16] to the US Army to improve the Q-127, also achieved a GSD $\simeq$ 1.15 with a very considered and sophisticated approach but could do no better except at low concentrations and flow rates. They developed and used a real-time measurement device (which uses a HeCd laser) which measures the GSD by observing the polarization ratio at two fixed scattering angles ($84°$ and $116°$).

The capability of the thermal generation process to produce monodisperse particles deserves further study. However, for the present purpose and as a first step, a candidate substitute material need only demonstrate comparable behavior in a side by side comparison with "DOP" in equivalent thermal generators. The ability to produce monodisperse particles is confounded with generator design and operation and complete resolution cannot be expected at this time.

The critical liquid physical properties controlling thermal generation are vapor pressure and thermal stability. The desired goal of monodispersity dictates the use of a relatively pure compound. In order to obtain a monodisperse aerosol, all particle growth (condensation) must start simultaneously, proceed at the same rate and arrive at the same final size. This is clearly impossible with a mixture of compounds having different vapor pressures. The candidate "DOP" substitutes of relevant interest are therefore the pure polyethylene glycols which are closest to "DOP" in vapor pressure (measured at some reasonable reference temperature). Vapor pressure/temperature data have been published for a series of pure glycols up

to tetraethylene glycol by Gallaugher and Hibbert[17]. Figure 1 below is a plot of estimates made from their data for the temperature achieving 5mm Hg vapor pressure for members of the series. A linear projection appears reasonable and indicates that a match of "DOP" performance should lie between pentaethylene glycol as a lower bound and hexaethylene glycol as an upper bound.

$$H-O-(CH_2-CH_2-O)_\eta - H$$
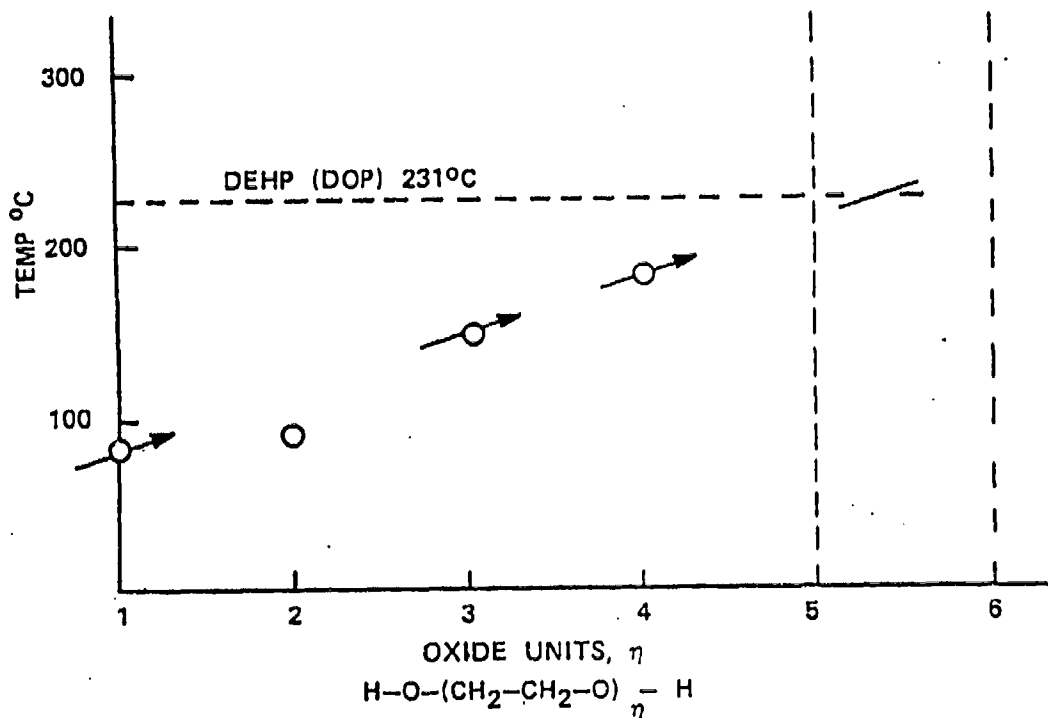
Figure 1: Oxide Units in Polyethylene Glycol vs. Estimated Temperature Achieving 5mm Hg Vapor Pressure

Either liquid should be useful if the appropriate generator controls can be varied to compensate for the differences. Pentaethylene glycol should make a test aerosol of acceptable concentration at a lower reservoir temperature than "DOP". Hexaethylene glycol will undoubtedly require a higher reservoir temperature. The count median diameter (CMD) and the geometric standard deviation (GSD) will be dependent on the control of the temperature gradients achievable in the condensation region of the specific generator in question.

Both pentaethylene glycol and hexaethylene glycol are difficult to obtain at present. Pentaethylene glycol purported to be 97% pure was procured from the Columbia Organic Chemical Company, Columbia, SC and used in the tests described herein. (Hexaethylene glycol was not received in time to be included in the tests.)

Experimental Procedure

Preparatory Tests (Sept 23, 1980)

Tests were conducted with the cooperation and facilities of the Occupational Safety and Health Products Division of the Tape Group of the 3M Company, St.Paul,MN.

The quality assurance section there has had several years experience with the Q-127 type machine made by ATI, Inc., Baltimore, MD. They have many machines at various plant sites including those at the St. Paul laboratory. They test the filter media and their product line of disposable respirators as part of the R&D process and for quality control and acceptance in the manufacturing process.

Two side-by-side Q-127 type machines of very recent manufacture were used for the present work. The machine used for testing the pentaethylene glycol was drained of "DOP" while still hot and allowed to cool. The reservoir was then flushed with methyl-ethyl-ketone, drained and blown dry with compressed air. Next, the reservoir was filled with tetraethylene glycol and drained. The reservoir was then filled with pentaethylene glycol and brought up to 170°C. ("DOP" is generated at 167°C in the St. Paul laboratory). All other machine controls were set at the standard levels for "DOP". Dense smoke was immediately made but initial indications from the owl and the aerosol laser spectrometer were that the particle size was much larger than desired. It was therefore decided to chill the compressed air (incoming dew point - 20°C) to lower the temperature in the condensation region of the machine. This was accomplished by constructing a jury-rigged heat exchanger using a length of compressed air hose coiled into a 5 gallon pail containing dry ice. Modifications were made to the Q-127 to allow insertion of thermometers into both the vapor pick-up and diluent air lines. Although the expedient dry ice technique appears drastic, the temperatures resulting in the vapor pick-up and diluent air lines are not unreasonable and appear easily achievable by more conventional laboratory and plant practices. As a further precaution, the machine was again drained and refilled with fresh pentaethylene glycol. At a reservoir temperature of 170°C the concentration was found to be in excess of 185 $\mu g/\ell$. (Concentration was measured conventionally by weighing a timed accumulation on an absolute filter pad with knowledge of the volume flow rate.) The reservoir temperature was therefore reduced and variations in flow rates and temperatures of the vapor pick-up and diluent air were tried in order to bring the apparent particle size (as indicated by the owl and the laser aerosol spectrometer) into the desired size range region.

Laser Aerosol Spectrometer

The Laser Aerosol Spectrometer Model ASAS-300A system made by Particle Measuring Systems, Inc., Boulder, CO (PMS) was used to determine particle size. The system had been calibrated the previous week with Dow polystyrene latex microspheres of known size. The validity of the calibration procedure and the insensitivity of the instrument to refractive index changes is discussed by Hinds, First, et. al.,[15] and by Knollenberg [18]. The ASAS-300 probe can measure particle diameter down to 0.15 μm in the lowest range. Procedures exist to merge the data when the measurements involve overlapping ranges.

For the present tests the instrument was modified for "in-line" sampling. The normal inlet horn was removed and replaced with a PMS supplied stream "focusser" with tubing connector. The normal integral suction fan was removed and replaced with a plug and tubing nipple. An aerosol "clean up" filter and rotameter was placed downstream of the instrument. A Gast Model 1531 vacuum pump was used to pull the smoke sample from the chuck of the Q-127 through the instrument train. Surgical tubing (3/8" OD) was used throughout for connections.

The validity of measurements using the laser aerosol spectrometer is very dependent on particle number concentration. A "by-pass" diluter was therefore used between the Q-127 chuck take off and the PMS instrument to achieve a count rate of about 100 counts per second. In the actual test, count data were

accumulated for about 30 seconds. The "by-pass" diluter splits the sampled stream into two fractions. One of the fractions is filtered and then remerged with the unfiltered fraction. The count rate can be varied using throttling valves and controlling the fraction of the flow which is filtered in relation to the unfiltered fraction.

Proof Testing (Sept 24, 1980)

Stable operation of the Q-127 with pentaethylene glycol was achieved in the desired concentration range. Mass concentrations in the range of 72-113 µg/ℓ were achieved over the reservoir temperature range of 145-150°C. The operating conditions are shown in Table II.

Table II: Q-127 Conditions Using Pentaethylene Glycol

Reservoir Temperature	145-150°C
Temperature Vapor Pickup Air	∿23°C
Temperature Diluent Air	∿17°C
Flow Rate Vapor Pickup Air	∿12 lpm
Flow Rate Diluent Air	∿85 lpm
"Heater" Variac Setting	∿34 div
"Particle Size" Variac Setting	∿17 div
Owl Setting	28-29°

Three sets of representative pentaethylene glycol particle size measurements as made with the PMS ASAS-300A laser aerosol spectrometer system are given in Table III and compared with two sets of representative "DOP" data.

Table III: Particle Size Count Comparison
Pentaethylene Glycol (PTAEG) vs. Di(2-ethylhexyl)
Phthalate Using PMS ASAS 300A Instrument

Instrument Channel	Instrument Range	Calibrated Midpoint Size, µm	"DOP" A	"DOP" B	PTAEG A	PTAEG B	PTAEG C
1	3	0.155	180	189	267	375	285
2	3	0.165	185	210	294	408	301
3	3	0.175	209	233	329	428	339
4	3	0.185	251	206	274	384	355
5	3	0.195	241	286	263	379	291
6	3	0.205	220	208	241	333	297
7	3	0.215	209	225	194	279	304
8	3	0.225	204	160	169	207	288

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Table III: (Cont.)

9	3	0.235	197	180	133	203	255
10	3	0.245	170	180	150	139	207
11	3	0.255	166	189	104	176	182
12	3	0.265	138	125	97	113	154
13	3	0.275	131	122	70	75	135
14	3	0.285	108	110	40	65	101
15	3	0.295	126	110	54	51	89
4	2	0.318	68	77	16	21	12
5	2	0.343	54	60	8	10	13
6	2	0.368	36	43	5	6	7
7	2	0.393	19	34	2	3	3
8	2	0.418	12	14	1	2	1
9	2	0.443	5	7	0	1	0
10	2	0.468	7	6	0	0	0
11	2	0.493	3	7	0	1	0
12	2	0.518	4	4	0	0	0
13	2	0.543	1	4	0	0	0
14	2	0.568	2	2	0	0	0
15	2	0.593	2	1	0	0	0

Particle Size Data Reduction

The PMS ASAS 300A probe can only sense particle diameter as low as 0.15 μm. It is evident from Table III that the size distribution was not completely determined since the instrument was not capable of measuring the lower end of the size spectrum. Initially, an heuristic method was developed to try to infer the missing data. That method was based on the premise that the mode of the distribution was contained in the measured data. It was clear that calculations based on the truncated data overestimated the count median diameter (CMD) and underestimated the geometric standard deviation (GSD). This is to be expected when the contribution of the smaller particle diameters are not included in the population. It is of interest to note that a linearized graphical estimation procedure using log-probability paper was more reliable in estimating the GSD than a purely computational procedure. The linearized graphical procedure is more satisfactory than computation when the distribution deviated from the assumption that the logs of the diameters are normally distributed. The standard computational procedure gives all points equal weight whereas in the linearized graphical procedure one ignores the deviations at the tails of the distributions. (The need for a weighting factor scheme similar to that used in some types of statistical bioassay is apparaent.

A search of the statistical literature uncovered the Pearson-Lee-Fisher (PLF) method [19] of extrapolating singly truncated normal distributions. The method was validated and programmed for the present purpose for the computer by Pennsyle[20].

Table IV presents the results of computation for the two sets of "DOP" size data and the three sets of PTAEG size data. The CMD and the GSD are given for both the measured truncated population (raw data) and the P-L-F corrected estimation.

Table IV: Count Median Diameter (CMD) and
Geometric Standard Deviation (GSD)
Estimates

Test	Based on Raw Data		P-L-F Corrected	
	CMD μm	GSD	CMD μm	GSD
"DOP" A	0.222	1.26	0.210	1.31
"DOP" B	0.223	1.27	0.206	1.34
PTAEG A	0.202	1.20	0.188	1.26
PTAEG B	0.200	1.20	0.186	1.26
PTAEG C	0.209	1.21	0.201	1.24

Owl Interpretation of Particle Size Distribution

Hinds, First, et. al. [15] showed that the polarization-ratio owl, when challenged with a distribution of particle sizes, indicates a weighted average particle size. The specific polarization ratio was estimated to vary with particle diameter to the 8.1 power. A numerical integration scheme was employed to compute values for the average polarization ratio, the components of which were calculated from the Mie theory. They showed that, for a true log-normal distribution, an infinite number of GSD-CMD pairs would yield an owl setting of 29°. However, it can be shown for log-normal distributions of particle size that simple relationships exist between the weighted average particle size and the CMD and GSD[21]. In particular, the average particle size weighted to the eighth power is related to the CMD and GSD as follows:

$$\ln \overline{d^8} = \ln \left[\frac{\Sigma n_j d_j^8}{\Sigma n_j} \right]^{\frac{1}{8}} = \ln \left[CMD \right] + 4 \ln^2 \left[GSD \right] \tag{1}$$

Table V shows the relationship between the GSD and CMD pairs used by Hinds, First, et. al.[15], (all of which yield an average particle size (d $\overline{PR}$) of 0.3 μm "seen by the owl at setting of 29°) and the value of $\overline{d^8}$ computed from equation (1) using the same pairs.

Table V: $\overline{d^8}$ vs. d $\overline{PR}$

GSD	CMD	$\overline{d^8}$	d $\overline{PR}$
1.00	0.300	0.300	0.300
1.05	0.294	0.297	0.300
1.10	0.286	0.297	0.300
1.15	0.274	0.296	0.300

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Table V: (Cont.)

1.20	0.260	0.297	0.300
1.25	0.246	0.300	0.300
1.30	0.230	0.302	0.300

It is concluded that the weighted average $\overline{d^8}$, gives results practically equivalent to d $_{\overline{PR}}$ and may be used to infer the average size "seen" by the owl when sampling a polydisperse aerosol whose diameters are log-normally distributed. Table VI gives the estimations made for the two "DOP" tests and the three PTAEG tests previously tabulated:

Table VI: Average Particle Size $\overline{d^8}$ "Seen" by Owl

P-L-F Corrected

Test	CMD μm	GSD	$\overline{d^8}$ μm
"DOP" A	0.210	1.31	0.281
"DOP" B	0.206	1.34	0.290
PTAEG A	0.188	1.26	0.233
PTAEG B	0.186	1.26	0.230
PTAEG C	0.201	1.24	0.242

Filter Penetration Comparisons

Several disposable half-face respirators manufactured by the 3M Company were tested on the side by side Q-127 machines respectively filled with pentaethylene glycol and "DOP". Two glass filter pads were also tested. The results are shown in Table VII.

Table VII: Comparative % Penetration Tests

Item	"DOP" % PEN.	PTAEG % PEN
Respirator # 1	24	23
Respirator # 2	32	27
Respirator # 3	10	10
Respirator # 4	10	10
Respirator # 5	1.27	1.1
Respirator # 6	24	24
Respirator # 7	1.37	1.24
Respirator # 8	1.26	1.11
Respirator # 9	4.44	4.0
Glass Fiber Filter A	3.7	3.1
Glass Fiber Filter B	0.08	0.06

Tetraethylene Glycol

Tetraethylene glycol is commercially available and relatively inexpensive. Time did not allow testing it during the program of September 23-24. However, it was later determined [22] that it would not make aerosol within the operating range of the Q-127 with any control over particle size and concentration.

Discussion of Results

Although additional tests are required before unequivocal conclusions can be drawn, it appears that pentaethylene glycol (PTAEG) shows good promise as a substitute for "DOP" in the thermal generation mode. Use of neither "DOP" nor PTAEG in the Q-127 machines at the 3M Company in St. Paul achieved the design goals of a count median diameter of 0.3 μm and a geometric standard deviation of 1.10. The lowest geometric standard deviation reported by others as achievable in the Q-127 is 1.15. However, the lowest (best estimate) during this test series was 1.24 using PTAEG (Table IV). The 3M Company standard operating procedures are scrupulous in attention to detail. The machines are even kept in a temperature controlled environment at 72°F. The compressed air is oil-free and has a dew-point of -20°C. Passing the compressed air through a particulate filter rated to retain sub-micron particles does appear to affect the resultant particle size distribution [23]. Means of controlling the GSD, therefore, remain a mystery. It is conceivable, however, that lack of control of condensation nuclei too small to be filtered by the particulate filters normally employed for compressed air service cause a variation in particle growth rate which then affects the GSD. The only known way of removing these nuclei is to condense liquid upon them and cause them to grow to a physically removable size. This is demonstrated in variable volume cloud chambers by saturating with water vapor and then cooling by sudden expansion of the volume. The water droplets condense on the nuclei and are removed by settling and/or filtration. The process is repeated ("pumping") until no nuclei are present. It is conceivable that this nuclei removal process or an equivalent process applied to the compressed air used for vapor pick-up and diluent air in the Q-127 might resolve the GSD problem. Control of the CMD, on the other hand, is much easier. Covariation of the mass concentration (reservoir temperature) and the temperature gradient in the condensation region of the Q-127 machine can usually result in the desired owl reading. However, the GSD is also affected by this procedure and without a real-time GSD "meter" one would not be aware of this. It is conceivable that with a real-time meter the GSD might be improved through proper setting of the Q-127 controls. The Arthur D. Little GSD meter [16] would be a very valuable addition to the Q-127 system for such a purpose. The manual owl version allowing observation over a scan of scattering angles to pick up the Higher Order Tyndall Spectra [24] produced by monodisperse aerosols might also serve the purpose. It would be slower in use than the A. D. Little instrument but would be much cheaper to make. Conceivably its operation could also be made faster by automating the coupled electro-optical and mechanical functions.

In perspective, it appears that the pentaethylene glycol shows excellent promise of substituting for "DOP" in thermal generation. In the side-by-side comparison with "DOP" the GSD was smaller and although the CMD was also smaller than desired, no difficulty is anticipated in increasing it. The limited schedule available for this program simply did not permit further work at this time and future tests are planned to acquire the additional information. The results of the side-by-side filter penetration tests are encouraging. There is an unexplained enigma, however, in that the smaller average particle size of the PTAEG always gave a somewhat lower penetration value than the larger average particle size of the "DOP". The only explanation so far conceived is the possible existence of a

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bimodality (skewed toward larger particles) in the particle size distribution which might not have been observed with the laser aerosol spectrometer. It would be very interesting to check the particle size distribution with another type of instrument having a larger range such as the quartz crystal micro-balance cascade impactor [25].

From a qualitative point of view, PTAEG is relatively odorless even when hot. "DOP" is odorless when disseminated cold but has a distinctive odor when disseminated hot. The smoke observed in the owl seemed brighter than "DOP" smoke at equivalent concentrations. Changes in the aerosol characteristics (size and concentration) seemed very responsive to changes in the Q-127 control settings. Except for an initial stabilization period (in which impurities were perhaps volatilized and purged), the PTAEG operation appeared more stable over time than the "DOP" operation. One unknown factor at this time is the stability of PTAEG under prolonged heating in the reservoir. The initially water-white material was slightly yellow when looked at after two days of operation. This must be investigated for longer periods in future tests.

Cost and Availability

Neither pentaethylene glycol nor hexaethylene glycol is easily available at present. PEG 200 which could be the feed-stock source of the pure compounds is available and very inexpensive (about $7/gallon in 55 gallon lots). Pentaethylene glycol represents 21% of the total weight in PEG 200 but requires extreme measures such as high vacuum distillation to effect separation. The Inland Vacuum Company of Rochester, NY, made a preliminary feasibility study of high vacuum distillation for recovery of PTAEG. They reported [26] that about 25% of the 21% PTAEG in PEG 200 might be recovered. However, two passes through their equipment are required at a feed rate of about two gallons/hour. Product purity has yet to be determined. Taking all factors into consideration, they believed that they could initially supply PTAEG at a cost of $500/gallon but that further process refinement and larger scale operation might conceivably lower the cost to the neighborhood of $200/gallon [27].

An alternative process which may be more efficient and thus faster is plant-scale liquid chromatography [28]. PEG 200 has been supplied to the domestic representative of the Elf Aquitaine Company of France for a feasibility determination and preliminary cost estimate. Results are not yet available.

Another avenue not yet explored is the possibility that pentaethylene or hexaethylene glycol might be produced by some optimized chemical reaction which would enable simple and inexpensive purification. Further exploration of this possibility is required.

In perspective, one must note that total present usage in the US of "DOP" for filter media and filter quality acceptance testing is probably less than 5000 gallons/year. Considering the limited alternatives (expensive ventilation equipment, personnel protection, environmental pollution control equipment) the additional operating cost may not be unreasonable. The cost of labor to operate and support the quality control and acceptance facilities will probably be a much higher element of operating cost than the cost of the pentaethylene glycol.

It should be noted that the comments made above are relevant only to operation of thermal generation ("monodisperse") equipment. The PEG 400 recommended for polydisperse aerosol generators is relatively inexpensive and cost should not be an important factor.

Conclusions

1. Based on the available toxicology data base for the polyethylene glycols, the probability appears high that PEG 400 and pentaethylene glycol (PTAEG) could receive approval by the Secretary, US Department of Health and Human Services or his designee (OSHA) as substitutes for "DOP" in the various filter, filter media, and respirator test roles.

2. Based on comparative tests performed (Sep 80) at Harvard Air Cleaning Laboratory, it appears that PEG 400 or a related mixture or blend acceptably matches "DOP" performance in polydisperse aerosol generators employing submerged atomization nozzles.

3. Based on comparative tests performed (Sep 80) at the 3M Company, it appears that PTAEG acceptably matches "DOP" performance, controllability, and stability in the Q-127 thermal generator and filter penetration measurement system.

4. PEG 400 and related mixtures or blends are relatively inexpensive (about $7/gallon) and widely available.

5. PTAEG is not easily available at present.

6. Although the present estimated cost of producing PTAEG is high ($200-$500/gal) its use might not be unreasonable considering the limited and expensive alternatives known at present.

7. Alternative production methods for PTAEG have been conceived and may result in a more reasonable cost.

8. Tetraethylene glycol which is widely available and relatively inexpensive could not be made to work in the Q-127.

Recommendations

1. Investigation of the use of pentaethylene glycol (PTAEG) as a "DOP" substitute should be expanded and continued. In particular the effects of continuous heating should be determined.

2. The need for "monodisperse" filter and media testing should be re-examined. New specifications and standards should be developed as appropriate.

3. New equipment should be developed to implement new standards as appropriate. Shortcomings of present equipment; e.g., continuous heating, should be eliminated.

4. If "monodisperse" testing continues to be the standard method, efforts should be made to determine the causes of GSD variations and control them with the hopeful outcome of achieving a GSD closer to 1.1.

5. If "monodisperse" testing continues to be the standard method, real-time GSD meters should be incorporated into the test systems.

6. The possibilities of producing PTAEG at lower cost should be intensively explored.

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7. The capabilities of hexaethylene glycol as a "DOP" substitute should be explored.

8. Requests should be submitted to the Secretary, US Department of Health and Human Services and to OSHA asking approval for the use of PEG 400 and PTAEG in their respective test roles.

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APPENDIX G

TOXICOLOGICAL SCREENING OF CANDIDATE

DOP REPLACEMENT MATERIALS

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TOXICOLOGICAL SCREENING OF CANDIDATE

DOP REPLACEMENT MATERIALS

Reference 4 of the main text includes a discussion of the process that was used to search for candidate materials to replace DOP by considering their toxicological and physical properties, and their likely environmental impact. This process is represented schematically in Figure G.1.

Physical property screening is discussed in Appendix H, and will not be considered further here.

Since inhalation is the principal route of entry, but dermal and oral routes must also be considered, materials were searched for minimal toxicity in these categories if, indeed, such data existed for materials of potential interest. Also, it was considered desirable that the smoke or its precursors should not have an unpleasant odor that would contaminate the facility or the operator's clothing.

A toxicological evaluation was conducted on the most promising materials identified during a search of chemical and physical properties. The results of the toxicology search are tabulated in Table G.1.

These show that among the materials or compounds in the data base that had low to moderate toxicities were the ethylene glycols and oleic acid. Data are also given for DOP and DOS, and for the tris phosphate containing the 2-ethylhexyl group that is suspect as a cause of carcinogenicity in such compounds.

The biological properties of DOS have been extensively reviewed under a contract with the Department of Energy; see: Silverstein, B.D., White, O., Brower, J.E., and Bernholc, N.M., Biological Effects Summary Report Di (2-Ethylhexyl) Sebacate, BNL 51729 UC41, Brookhaven National Laboratories, Upton, New York, October 1983.

Recent guidance to the U.S. Army Research, Development and Engineering Center (CRDEC) has indicated that DOS should not be considered further as a replacement material for DOP, since it is likely that DOS also will be added to the growing list of suspect carcinogens.

Another class of compounds that is believed to exhibit low toxicity are the straight chain alkanes. These are discussed further in Appendix H and in the text.
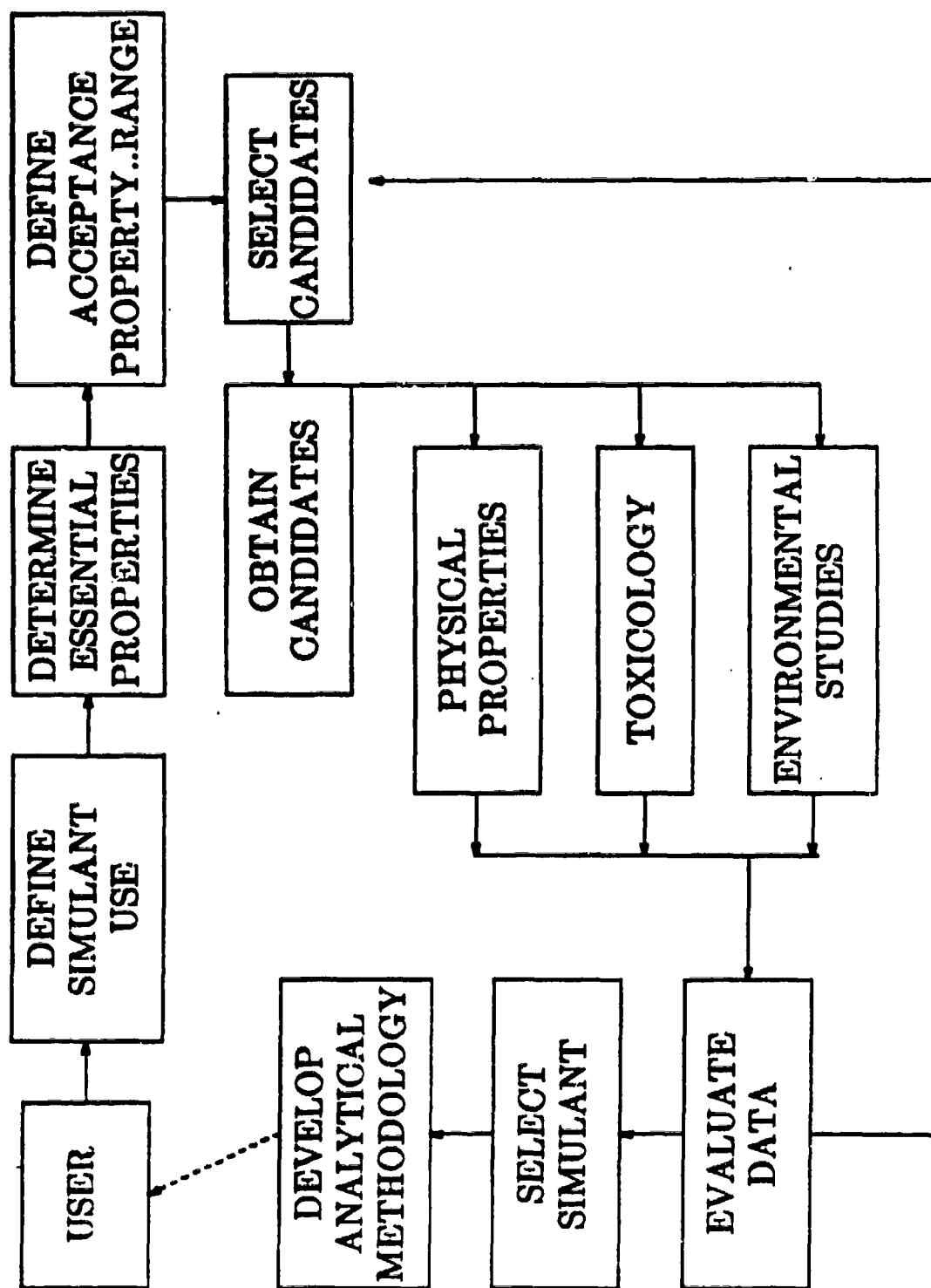
Figure G.1   Candidate Replacement Material Selection Process.

COMPOUND	RAT (ORAL) LD_{50}	RABBIT	MOUSE	HUMAN	OTHER
Tetraethylene glycol	29 g/kg	Eye irritant		Mod skin/eye irritant (RTECS)	
Hexaethylene glycol	32 g/kg	No eye irritation		Non-irritating Skin/Eye Irritant (RTECS)	
PEG 200	28 g/kg	LD_{50}(oral) 14 g/kg	LD_{50}(oral) 34 g/kg		
Oleic Acid	74 g/kg	Mild Skin Irritant	LD_{50}(iv) 230 mg/kg	Moderate irritation 0.18mg/3days on skin	Tumorigenic (Rat) Tumor Promoter
Di(2-ethylhexyl) sebacate	12.8 g/kg	LD_{50}(iv) 540 mg/kg	LD_{50}(oral) 9.5 g/kg		
Bis-(2-ethylhexyl) phosphate	4.9 g/kg	LD_{50}(pc) 1.2g/kg 5mg = Med Eye Irritation	LD_{Lo}(ip) 63mg/kg		
Tris-(2-ethylhexyl) phosphate	37 g/kg	LD_{Lo}(pc) 20 g/kg			Tumorigenic (rat)

Table G.1   Toxicity of Possible Replacement Materials.

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APPENDIX H

PHYSICAL PROPERTY SCREENING OF CANDIDATE

DOP REPLACEMENT MATERIALS

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PHYSICAL PROPERTY SCREENING OF CANDIDATE

DOP REPLACEMENT MATERIALS

The process of candidate replacement material screening based on physical properties was indicated in Figure G.1. of Appendix G. and has been discussed in some detail in the text of the main report.

The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) Simulant Data Center was created as a repository for simulant information that facilitates retrieval based on numerical data for 40 chemical and physical properties of hundreds of compounds. Those compounds whose properties fall within a designated range of properties, either singularly or in combination, thus can be selected.

When only a few physical property data are available for properties such as normal boiling point, vapor pressure, water solubility, surface tension and liquid viscosity, data can be extrapolated with a good degree of accuracy using various proven models and estimation techniques.

Chemical structure of possible replacement materials is important not only from a toxicological standpoint, but because many candidate materials are members of families of compounds whose physical properties vary in an orderly way as the molecular weight is increased or decreased, and thus can be modeled effectively. Structures of some possible replacements for DOP are shown in Table H.1.

In Table H.2., representative physical properties of some possible replacement materials for DOP are given. In Table H.3., many physical properties of selected straight-chain alkanes, separated by only one carbon in their chains, are tabulated. It can be seen quite clearly that selection of most promising candidate materials for use in a given smoke penetrometer machine is greatly facilitated by such tabulated information.

Other examples of candidate screening by physical properties are given in the main text of this report. The discussion of candidate materials actually tested in this program follows the format of compounds within families, evaluated by order of increasing or decreasing molecular weight.

Chemical Name	Formula
Dioctyl phthalate	$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2\text{-}C_6H_4$
Dibutyl phthalate	$C_6H_4[C(O)OC_4H_9]_2$
Diisooctyl phthalate	$C_6H_4[C(O)OC_6H_{12}CH(CH_3)_2]_2$
Tetraethylene glycol	$HO\text{-}(CH_2CH_2O)_4H$
Pentaethylene glycol	$HO\text{-}(CH_2CH_2O)_5H$
Hexaethylene glycol	$HO\text{-}(CH_2CH_2O)_6H$
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Bis-(2-ethylhexyl) sebacate	$[CH_3(CH_2)_3CH(C_2H_5)CH_2OC(O)C_4H_8\text{-}]_2$
Bis-(2-ethylhexyl) phosphate	$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2P(O)OH$
Tris-(2-ethylhexyl) phosphate	$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_3PO$
PEG 200	mixture
Erythritol	$HO\text{-}CH_2[CH(OH)]_2CH_2OH$
Pentaerythritol	$C(CH_2OH)_4$

Table H.1 Chemical Structures of Possible Replacement Materials.

Chemical Name	MW	BP	Vapor Pressure @ 20°C	Viscosity @ 20°C	Surface Te @ 20°C
Dioctyl phthalate	390	384	7.1×10^{-8}	79	33
Dibutyl phthalate	278	340	1.5×10^{-5}	19.7	33.4
Diisooctyl phthalate	390		3.0×10^{-7}	83.0	32.3
Tetraethylene glycol	194	314	7.8×10^{-6}	55.0	46.1
Oleic acid	282	441est	1.1×10^{-5}	38.8	32.8
Bis-(2-ethylhexyl) sebacate	426	462	1.3×10^{-8}	41.4	39.5
Bis-(2-ethylhexyl) phosphate	322	431	2.0×10^{-8}	6.5	33
Tris-(2-ethylhexyl) phosphate	434	395est	6.5×10^{-8}	14.1	31.0
PEG 200	~200	~307			56
Erythritol	122	330	3.2×10^{-5}		
Pentaerythritol	136	370 est	2.0×10^{-6}		

Table H.2   Physical Properties of Possible Replacement Materials.

$$CH_3-(CH_2)_{n-2}-CH_3$$

n	Name	MW	MP (°C)	BP at 1 atm (°C)	VP at 20°C (10^{-8} torr) (Est.)	VP at 200°C (torr) (Est.)	Viscosity at 20°C (centipoise) (Est.)	ST at 20°C (dynes/cm^2) (Est.)	Density (g/ml)
20	Eicosane	282	36.8	343	130	14	7.0	28.6	.79
21	Heneicosane	296	40.5	356	59	9	8.3	28.9	.79
22	Docosane	310	44.4	369	27	6	9.9	29.0	.79
23	Tricosane	324	47.6	380	14	4	11.8	29.2	.79
24	Tetracosane	338	54	394	6	3	14.1	29.5	.80
25	Pentacosane	352	-	402	3.6	2.4	16.7	29.6	.80
26	Hexacosane	366	56.4	412	1.9	1.7	19.6	29.7	.80
	DOP	390	-	384	4.5	1.2	70	33	.98

Table H.3   Selected Straight Chain Alkanes.

APPENDIX I

SELECTED EXPERIMENTAL DATA

AND RESULTS

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SELECTED EXPERIMENTAL DATA

AND RESULTS

In this appendix, strip charts from the HP-85 Microcomputer (Appendixes E and J) used with the LAS-X Laser Aerosol Spectrometer are reproduced at 75% of their original dimensions. Each chart contains data in four size ranges, each containing 15 "bins" for which the particle diameters (μm) sampled are shown. The table at the top of each chart includes aerosol number concentration, geometric mean diameter, and geometric standard deviation (σ_g) based on the computed fit (dashed curve) for the measured particle size distribution shown in the figure. Certain assumptions are made in the computations which are discussed in Appendix J.

The data shown are representative, and include results for samples of DOP, DOS, and a variety of candidate materials that were found to be promising. It can be seen, for example, that DOP itself does not perform as well in the penetrometer machines as do several of the candidate replacement materials.

Although the approved Test Plan (Appendix C) called for aerosols with a 0.3 μm geometric mean diameter (GMD) and a σ_g less than 1.3, in the experimental procedure it was standard practice to attempt to generate aerosols ranging in mean diameter from 0.2 to 0.3 μm (since recent recommendations for penetrometer operation include the use of particles smaller than 0.3 μm because these are more effective in penetrating modern filters than are larger particles).

Thus some of the data included in the tables here are for particle diameters of 0.2 μm or slightly less, while others are in the size range closer to 0.3 μm. In some cases the performance of a candidate material changed significantly across this diameter range, particularly the σ_g values (see Tables D.2. and E.1. in Appendixes D and E, respectively.

On each page, the penetrometer machine used and its operating settings are indicated. Aerosol characteristics also are given (these can be seen as well in the top table of each chart

```
PROBE RANGE=2    TOT CNTS=   4?01
BIN   DIA     COUNT   DISTN VALUE
 0    .170      64    2.58E+001
 1    .200     167    5.97E+001
 2    .230     569    2.32E+002
 3    .260    1033    4.73E+002
 4    .290    1037    5.27E+002
 5    .320     737    4.11E+002
 6    .350     394    2.40E+002
 7    .380     177    1.16E+002
 8    .410      57    4.04E+001
 9    .440      11    8.34E+000
10    .470       4    3.23E+000
11    .500       3    2.57E+000
12    .530       4    3.63E+000
13    .560       0    0.00E+000
14    .590       1    1.01E+000
      .620  (       23=OVERCOUNT)
```

```
PROBE RANGE=1    TOT CNTS=   2215
BIN   DIA     COUNT   DISTN VALUE
 0    .300    2046    3.56E+002
 1    .400     145    3.25E+001
 2    .500       7    1.92E+000
 3    .600       2    6.49E-001
 4    .700       3    1.12E+000
 5    .800       0    0.00E+000
 6    .900       4    1.90E+000
 7   1.000       1    5.25E-001
 8   1.100       4    2.30E+000
 9   1.200       0    0.00E+000
10   1.300       0    0.00E+000
11   1.400       2    1.45E+000
12   1.500       0    0.00E+000
13   1.600       0    0.00E+000
14   1.700       1    8.75E-001
     1.800  (         0=OVERCOUNT)
```

```
PROBE RANGE=0    TOT CNTS=      1
BIN   DIA     COUNT   DISTN VALUE
 0   1.500       1    2.12E-001
 1   1.900       0    0.00E+000
 2   2.300       0    0.00E+000
 3   2.700       0    0.00E+000
 4   3.100       0    0.00E+000
 5   3.500       0    0.00E+000
 6   3.900       0    0.00E+000
 7   4.300       0    0.00E+000
 8   4.700       0    0.00E+000
 9   5.100       0    0.00E+000
10   5.500       0    0.00E+000
11   5.900       0    0.00E+000
12   6.300       0    0.00E+000
13   6.700       0    0.00E+000
14   7.100       0    0.00E+000
     7.500  (         0=OVERCOUNT)
```

```
DATE 88/11/22   TIME 104240   FSLP
MAX CNTS/SEC=    430   SEC=    10
R:0-3 TPUN  0 BINS    2.00 ML/SEC
DILUTION RATIO            = 1.000E+000
TEMPERATURE        (C)=  2.200E+001
ATM PRESSURE (mm Hg)=  7.600E+002
REL HUMIDITY       (%)=  5.000E+001
A PARAMETER              = 0.000E+000
B PARAMETER              = 0.000E+000
C PARAMETER              = 0.000E+000
NUM CONC  (NUMB/cm3)= 2.227E+005
GEOM MEAN DIAM  (um)= 2.883E-001
GEOM STANDARD DEV    = 1.282E+000
MASS CONC    (mg/m3)= 3.974E-003
UNDIL MASSCON(mg/m3)= 3.974E-003
MAX CNTS/SEC          = 4.301E+002
PEAK DIAMETER (um)   = 3.046E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-008
FIT GEOM STAND DEV   = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

```
PROBE RANGE=3    TOT CNTS=   4264
BIN   DIA     COUNT   DISTN VALUE
 0    .120     101    1.04E+002
 1    .126      36    3.87E+001
 2    .132      18    2.02E+001
 3    .138      12    1.41E+001
 4    .144      10    1.22E+001
 5    .150      10    1.27E+001
 6    .156       8    1.06E+001
 7    .162      10    1.37E+001
 8    .168       8    1.14E+001
 9    .174      11    1.62E+001
10    .180       8    1.22E+001
11    .186       9    1.42E+001
12    .192      14    2.27E+001
13    .198      14    2.34E+001
14    .204      25    4.31E+001
      .210  (    3970=OVERCOUNT)
```

Machine: LAMAPP
Geometric Mean Diameter (μm): 0.2883
Geometric Standard Deviation (σ_g): 1.282
NaCl Solution Pressure (psi): 3.5
Candidate Liquid Pressure (psi): 2.0
Aerosol Dilution Air (lpm): 25
Tube Temperature (°C): 170

Table I.1   Performance of Emery 3002 Synthetic Hydrocarbon
in the LAMAPP Machine.

```
PROBE RANGE=2    TOT CNTS=   3010
BIN  DIA    COUNT   DISTN VALUE
 0   .170    1436    1.77E+002
 1   .200    1185    1.70E+002
 2   .230     291    4.75E+001
 3   .260      54    9.89E+000
 4   .290      21    4.27E+000
 5   .320       7    1.56E+000
 6   .350       2    4.86E-001
 7   .380       2    5.26E-001
 8   .410       1    2.83E-001
 9   .440       1    3.03E-001
10   .470       0    0.00E+000
11   .500       1    3.43E-001
12   .530       0    0.00E+000
13   .560       0    0.00E+000
14   .590       1    4.03E-001
     .620  <       0=OVERCOUNT)

PROBE RANGE=1    TOT CNTS=     36
BIN  DIA    COUNT   DISTN VALUE
 0   .300      24    1.67E+000
 1   .400       4    3.59E-001
 2   .500       0    0.00E+000
 3   .600       0    0.00E+000
 4   .700       2    3.00E-001
 5   .800       1    1.70E-001
 6   .900       2    3.80E-001
 7  1.000       2    4.20E-001
 8  1.100       1    2.30E-001
 9  1.200       1    2.50E-001
10  1.300       0    0.00E+000
11  1.400       0    0.00E+000
12  1.500       1    3.10E-001
13  1.600       0    0.00E+000
14  1.700       0    0.00E+000
    1.900  <       0=OVERCOUNT)

PROBE RANGE=0    TOT CNTS=      1
BIN  DIA    COUNT   DISTN VALUE
 0  1.500       0    0.00E+000
 1  1.900       0    0.00E+000
 2  2.300       0    0.00E+000
 3  2.700       1    1.45E-001
 4  3.100       0    0.00E+000
 5  3.500       0    0.00E+000
 6  3.900       0    0.00E+000
 7  4.300       0    0.00E+000
 8  4.700       0    0.00E+000
 9  5.100       0    0.00E+000
10  5.500       0    0.00E+000
11  5.900       0    0.00E+000
12  6.300       0    0.00E+000
13  6.700       0    0.00E+000
14  7.100       0    0.00E+000
    7.500  <       0=OVERCOUNT)
```

```
DATE YY/MM/DD  TIME 110720  PSLF
MAX CNTS/SEC=   342   SEC=    10
P-0-3 TRUN  0 BINS   5.00 ML/SEC
DILUTION RATIO       = 1.000E+000
TEMPERATURE     (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY    (%)= 5.000E+001
A PARAMETER          = 0.000E+000
B PARAMETER          = 0.000E+000
C PARAMETER          = 0.000E+000
NUM CONC  (NUMB/cm3)= 7.245E+001
GEOM MEAN DIAM  (um)= 1.992E-001
GEOM STANDARD DEV   = 1.202E+000
MASS CONC   (mg/m3)= 7.180E-004
UNDIL MASSCON(mg/m3)= 7.180E-004
MAX CNTS/SEC        = 3.420E+002
PEAK DIAMETER (um)  = 2.010E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-006
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL MO (mg.m3)= 0.000E+000

PROBE RANGE=3    TOT CNTS=   3420
BIN  DIA    COUNT   DISTN VALUE
 0   .120      64    2.62E+001
 1   .126      40    1.72E+001
 2   .132      42    1.89E+001
 3   .138      32    1.50E+001
 4   .144      27    1.32E+001
 5   .150      44    2.24E+001
 6   .156      37    1.96E+001
 7   .162      69    3.79E+001
 8   .168     111    6.33E+001
 9   .174     174    1.03E+002
10   .180     309    1.88E+002
11   .186     376    2.37E+002
12   .192     381    2.48E+002
13   .198     394    2.64E+002
14   .204     359    2.48E+002
     .210  <     961=OVERCOUNT)
```

Machine: LAMAPP
Geometric Mean Diameter (μm): 0.1992
Geometric Standard Deviation (σ_g): 1.202
NaCl Solution Pressure (psi): 6.0
Candidate Liquid Pressure (psi): 3.0
Aerosol Dilution Air (lpm): 50
Bypass Air (lpm): 1.0
Tube Temperature (^{O}C): 165

Table I.2   Performance of Emersol 875 Isostearic Acid
in the LAMAPP Machine.

Table I-3. Title

PROBE RANGE=2   TOT CNTS=   5841

BIN	DIA	COUNT	DISTN VALUE
0	.170	51	3.14E+001
1	.200	75	5.37E+001
2	.230	419	3.42E+002
3	.260	1201	1.10E+003
4	.290	1705	1.73E+003
5	.320	1370	1.48E+003
6	.350	639	7.77E+002
7	.380	264	3.47E+002
8	.410	105	1.49E+002
9	.440	22	3.34E+001
10	.470	11	1.78E+001
11	.500	3	5.15E+000
12	.530	1	1.82E+00?
13	.560	4	7.66E+000
14	.590	1	2.02E+000
	.620	<	10=OVERCOUNT)

PROBE RANGE=1   TOT CNTS=   3802

BIN	DIA	COUNT	DISTN VALUE
0	.300	3544	1.23E+003
1	.400	236	1.06E+002
2	.500	9	4.94E+000
3	.600	4	2.59E+000
4	.700	1	7.49E-001
5	.800	2	1.70E+000
6	.900	1	9.49E-001
7	1.000	1	1.05E+000
8	1.100	1	1.15E+000
9	1.200	1	1.25E+000
10	1.300	0	0.00E+000
11	1.400	1	1.45E+000
12	1.500	0	0.00E+000
13	1.600	0	0.00E+000
14	1.700	0	0.00E+000
	1.800	<	1=OVERCOUNT)

PROBE RANGE=0   TOT CNTS=   1

BIN	DIA	COUNT	DISTN VALUE
0	1.500	0	0.00E+000
1	1.900	0	0.00E+000
2	2.300	0	0.00E+000
3	2.700	0	0.00E+000
4	3.100	0	0.00E+000
5	3.500	0	0.00E+000
6	3.900	0	0.00E+000
7	4.300	0	0.00E+000
8	4.700	0	0.00E+000
9	5.100	0	0.00E+000
10	5.500	0	0.00E+000
11	5.900	0	0.00E+000
12	6.300	0	0.00E+000
13	6.700	0	0.00E+000
14	7.100	0	0.00E+000
	7.500	<	1=OVERCOUNT)

```
DATE 88/11/30   TIME 100830   PSLF
MAX CNTS/SEC=   595    SEC=   10
R.0-3 TRUN  0 BINS   1.00 ML/SEC
DILUTION RATIO           = 1.000E+000
TEMPERATURE        (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY       (%)= 5.000E+001
A PARAMETER          = 0.000E+000
B PARAMETER          = 0.000E+000
C PARAMETER          = 0.000E+000
NUM CONC (NUMB/cm3)= 5.909E+002
GEOM MEAN DIAM (μm)= 3.065E-001
GEOM STANDARD DEV  = 1.207E+000
MASS CONC    (mg/m3)= 1.057E-002
UNDIL MASSCON(mg/m3)= 1.057E-002
MAX CNTS/SEC         = 5.954E+002
PEAK DIAMETER (μm)  = 3.046E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (μm)= 1.000E-006
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

PROBE RANGE=3   TOT CNTS=   5954

BIN	DIA	COUNT	DISTN VALUE
0	.120	30	1.02E+002
1	.126	15	3.22E+001
2	.132	7	1.57E+001
3	.138	8	1.88E+001
4	.144	5	1.22E+001
5	.150	8	2.04E+001
6	.156	7	1.85E+001
7	.162	6	1.65E+001
8	.168	3	8.55E+000
9	.174	5	1.47E+001
10	.180	7	2.13E+001
11	.186	2	6.30E+000
12	.192	5	1.62E+001
13	.198	5	1.67E+001
14	.204	11	3.79E+001
	.210	<	5810=OVERCOUNT)

Machine: LAMAPP
Geometric Mean Diameter (μm): 0.3065
Geometric Standard Deviation (σ_g): 1.207
NaCl Solution Pressure (psi): 3.6
Candidate Liquid Pressure (psi): 2.0
Aerosol Dilution Air (lpm): 50
Tube Temperature (°C): 135

Table I.3   Performance of Emery 2219 Methyl Oleate Stearate in the LAMAPP Machine.

```
PROBE RANGE=2    TOT CNTS=   3241
BIN  DIA     COUNT   DISTN VALUE
 0   .170     803    4.94E+002
 1   .200    1223    8.77E+002
 2   .230     651    5.15E+002
 3   .260     281    1.57E+002
 4   .290     167    1.09E+002
 5   .320      55    6.14E+001
 6   .350      49    5.96E+001
 7   .380      20    2.63E+001
 8   .410      11    1.56E+001
 9   .440       8    1.21E+001
10   .470      10    1.62E+001
11   .500       3    5.15E+000
12   .530       7    1.27E+001
13   .560       3    5.75E+000
14   .590       1    2.02E+000
     .620  (     29=OVERCOUNT)
```

```
PROBE RANGE=1    TOT CNTS=    721
BIN  DIA     COUNT   DISTN VALUE
 0   .300     244    8.48E+001
 1   .400      32    1.43E+001
 2   .500      11    5.03E+000
 3   .600      10    6.49E+000
 4   .700       9    6.74E+000
 5   .800       4    3.40E+000
 6   .900       2    1.90E+000
 7  1.000       1    1.05E+000
 8  1.100       3    3.45E+000
 9  1.200       2    2.50E+000
10  1.300       1    1.35E+000
11  1.400       0    0.00E+000
12  1.500       2    3.10E+000
13  1.600       0    0.00E+000
14  1.700       0    0.00E+000
    1.800  (      0=OVERCOUNT)
```

```
DATE 88.10/7    TIME 174520   PSLF
MAX CNTS/SEC=   758    SEC=     10
P(0-3 TRUN   0 BINS     1.00 ML/SEC
DILUTION RATIO          = 1.000E+000
TEMPERATURE        (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY      (%)= 5.000E+001
A PARAMETER            = 0.000E+000
B PARAMETER            = 0.000E+000
C PARAMETER            = 0.000E+000
NUM CONC   (NUMB/cm3)= 3.664E+002
GEOM MEAN DIAM   (um)= 2.172E-001
GEOM STANDARD DEV    = 1.317E+000
MASS CONC    (mg/m3)= 5.093E-003
UNDIL MASSCON(mg/m3)= 5.093E-003
MAX CNTS/SEC        = 2.581E+002
PEAK DIAMETER (um)  = 2.070E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-006
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

```
PROBE RANGE=0    TOT CNTS=      3
BIN  DIA     COUNT   DISTN VALUE
 0  1.500       1    4.23E-001
 1  1.900       2    1.05E+000
 2  2.300       0    0.00E+000
 3  2.700       0    0.00E+000
 4  3.100       0    0.00E+000
 5  3.500       0    0.00E+000
 6  3.900       0    0.00E+000
 7  4.300       0    0.00E+000
 8  4.700       0    0.00E+000
 9  5.100       0    0.00E+000
10  5.500       0    0.00E+000
11  5.900       0    0.00E+000
12  6.300       0    0.00E+000
13  6.700       0    0.00E+000
14  7.100       0    0.00E+000
    7.500  (      0=OVERCOUNT)
```

```
PROBE RANGE=3    TOT CNTS=   3581
BIN  DIA     COUNT   DISTN VALUE
 0  .120      74    1.52E+002
 1  .126      53    1.14E+002
 2  .132      55    1.24E+002
 3  .138      53    1.23E+002
 4  .144      57    1.40E+002
 5  .150      63    1.75E+002
 6  .156      63    1.38E+001
 7  .162      67    1.84E+002
 8  .168      67    1.21E+002
 9  .174      75    1.54E+002
10  .180     107    1.26E+002
11  .186     171    5.39E+002
12  .192     214    5.35E+002
13  .198     245    6.21E+002
14  .204     279    5.62E+002
    .210  (   1977=OVERCOUNT)
```

Machine: LAMAPP
Geometric Mean Diameter (μm): 0.2172
Geometric Standard Deviation (σ_g): 1.317
NaCl Solution Pressure (psi): 5.0
Candidate Liquid Pressure (psi): 3.0
Aerosol Dilution Air (lpm): 35
Tube Temperature (°C): 165

Table I.4   Performance of Emery 3004 Synthetic Hydrocarbon
in the LAMAPP Machine.

ΔNUMCON/Δln(d) (×10-3)

DIAMETER (μm)
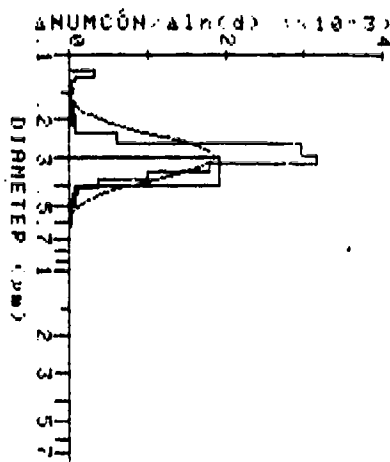
```
DATE 88/7/20   TIME 141320  PSLF
MAX CNTS/SEC=  1038   SEC=   10
R:0-3 TRUN  0 BINS   1 00 ML/SEC
DILUTION RATIO      = 1.000E+000
TEMPERATURE   (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7 600E+002
REL HUMIDITY    (%)= 5 000E+001
A PARAMETER         = 0.000E+000
B PARAMETER         = 0.000E+000
C PARAMETER         = 0.000E+000
NUM CONC   (NUMB/cm3)= 1.061E+003
GEOM MEAN DIAM   (μm)= 2.975E-001
GEOM STANDARD DEV   = 1.256E+000
MASS CONC   (mg/m3)= 2.182E-002
UNDIL MASSCON(mg/m3)= 2.182E-002
MAX CNTS/SEC        = 1.038E+003
PEAK DIAMETER  (μm)  = 3.046E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (μm)= 1 000E-008
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0 000E+000
```

PROBE RANGE=3   TOT CNTS= 10175

BIN	DIA	COUNT	DISTN VALUE
0	.120	158	3.24E+002
1	.126	39	9.38E+001
2	.132	20	4.50E+001
3	.138	17	3.99E+001
4	.144	21	5.14E+00
5	.150	17	4.33E+01
6	.156	10	2.65E+001
7	.162	13	3.57E+001
8	.168	23	5.55E+001
9	.174	12	3.54E+001
10	.180	13	3.96E+001
11	.186	16	5.04E+001
12	.192	26	8.45E+001
13	.198	16	5.36E+001
14	.204	16	5.52E+001
	.210 (	9758=OVERCOUNT)	

PROBE RANGE=2   TOT CNTS= 10377

BIN	DIA	COUNT	DISTN VALUE
0	.170	121	7 45E+001
1	.200	110	7.87E+001
2	.230	751	4 13E+002
3	.260	3231	2.96E+003
4	.290	3116	3 17E+003
5	.320	1594	1.78E+003
6	.350	830	1 01E+003
7	.380	296	3.90E+002
8	.410	79	1 12E+002
9	.440	39	5 91E+001
10	.470	20	3 23E+001
11	.500	15	2.57E+001
12	.530	11	2 00E+001
13	.560	14	2.68E+001
14	.590	18	3.63E+001
	.620 (	132=OVERCOUNT)	

PROBE RANGE=1   TOT CNTS=   5932

BIN	DIA	COUNT	DISTN VALUE
0	.300	5548	1.93E+003
1	.400	210	9.41E+001
2	.500	57	3.13E+001
3	.600	35	2.27E+001
4	.700	24	1.80E+001
5	.800	16	1.36E+001
6	.900	10	9 49E+000
7	1.000	9	9.44E+000
8	1.100	9	1 03E+001
9	1.200	4	5 00E+000
10	1.300	4	5.40E+000
11	1.400	3	4.35E+000
12	1.500	0	0.00E+000
13	1.600	0	0.00E+000
14	1.700	2	3 50E+000
	1.800 (	1=OVERCOUNT)	

PROBE RANGE=0   TOT CNTS=   6

BIN	DIA	COUNT	DISTN VALUE
0	1.500	6	2.54E+000
1	1.900	0	0.00E+000
2	2.300	0	0.00E+000
3	2.700	0	0.00E+000
4	3.100	0	0.00E+000
5	3.500	0	0.00E+000
6	3.900	0	0.00E+000
7	4.300	0	0.00E+000
8	4.700	0	0.00E+000
9	5.100	0	0.00E+000
10	5.500	0	0.00E+000
11	5.900	0	0.00E+000
12	6.300	0	0.00E+000
13	6.700	0	0.00E+000
14	7.100	0	0.00E+000
	7.500 (	0=OVERCOUNT)	

Machine: LAMAPP
Geometric Mean Diameter (μm): 0.2975
Geometric Standard Deviation (σ_g): 1.256
NaCl Solution Pressure (psi): 9.5
Candidate Liquid Pressure (psi): 4.0
Aerosol Dilution Air (lpm): 70
Tube Temperature (°C): 156

Table I.5   Performance of DOP in the LAMAPP Machine.

```
PROBE RANGE=2   TOT CNTS=   155?
BIN   DIA    COUNT   DISTN VALUE
 0    .170      19    1 17E+001
 1    .200      10    1 43E+001
 2    .230      79    6 44E+001
 3    .260     35?    3 27E+002
 4    .290     553    5 62E+002
 5    .320     479    5 37E+002
 6    .350     199    2 42E+002
 7    .380      63    8 29E+001
 8    .410      40    5 66E+001
 9    .440      13    1 82E+001
10    .470       5    9 70E+000
11    .500      11    1 39E+001
12    .530      10    1 83E+001
13    .560       2    3 83E+000
14    .590       2    4 03E+000
      .620  (      5=OVERCOUNT)
```

```
PROBE RANGE=1   TOT CNTS=   1273
BIN   DIA    COUNT   DISTN VALUE
 0    .300    1179    4 10E+002
 1    .400      70    3 14E+001
 2    .500      19    1 04E+001
 3    .600       5    3 24E+000
 4    .700       0    0 00E+000
 5    .800       0    0 00E+000
 6    .900       0    0 00E+000
 7   1.000       0    0 00E+000
 8   1.100       0    0 00E+000
 9   1.200       0    0 00E+000
10   1.300       0    0 00E+000
11   1.400       0    0 00E+000
12   1.500       0    0 00E+000
13   1.600       0    0 00E+000
14   1.700       0    0 00E+000
     1.800  (     0=OVERCOUNT)
```

```
PROBE RANGE=0   TOT CNTS=      0
BIN   DIA    COUNT   DISTN VALUE
 0   1.500       0    0 00E+000
 1   1.900       0    0 00E+000
 2   2.300       0    0 00E+000
 3   2.700       0    0 00E+000
 4   3.100       0    0 00E+000
 ?   3.500       0    0 00E+000
 6   3.900       0    0 00E+000
 7   4.300       0    0 00E+000
 8   4.700       0    0 00E+000
 9   5.100       0    0 00E+000
10   5.500       0    0 00E+000
11   5.900       0    0 00E+000
12   6.300       0    0 00E+000
13   6.700       0    0 00E+000
14   7.100       0    0 00E+000
     7.500  (     0=OVERCOUNT)
```

```
DATE 88/9/12   TIME 111110   PSLF
MAX CNTS/SEC=    197  SEC=    10
R:0-3 TRUN   0 BINS   1.00 ML/SEC
DILUTION RATIO           = 1 000E+000
TEMPERATURE        (C)= 2 200E+001
ATM PRESSURE (mm Hg)= 7 600E+002
REL HUMIDITY       (%)= 5 000E+001
A PARAMETER        = 0 000E+000
B PARAMETER        = 0 000E+000
C PARAMETER        = 0 000E+000
NUM CONC  (NUMB/cm3)= 1 930E+002
GEOM MEAN DIAM   (um)= 3 054E-001
GEOM STANDARD DEV  = 1 254E+000
MASS CONC    (mg/m3)= 3 473E-003
UNDIL MASSCON(mg/m3)= 3 473E-003
MAX CNTS/SEC       = 1 972E+002
PEAK DIAMETER (um)  = 3 046E-001
FIT NUM CONC (#/cm3)= 0 000E+000
FIT GEOM MN DIA (um)= 1 000E-008
FIT GEOM STAND DEV  = 1 000E+002
FIT UNDIL M0 (mg/m3)= 0 000E+000
```

```
PROBE RANGE=3   TOT CNTS=   1972
BIN   DIA    COUNT   DISTN VALUE
 0    .120      33    6 76E+001
 1    .126       8    1 72E+001
 2    .132       5    1 12E+001
 3    .138       4    9 40E+000
 4    .144       6    1 47E+001
 5    .150       4    1 02E+001
 6    .156       6    1 59E+001
 7    .162       5    1 37E+001
 8    .168       5    1 42E+001
 9    .174       4    1 18E+001
10    .180       4    1 22E+001
11    .186       5    1 57E+001
12    .192       2    6 50E+000
13    .198       4    1 34E+001
14    .204       5    1 72E+001
      .210  (   1872=OVERCOUNT)
```

Machine: Q127
Geometric Mean Diameter (μm): 0.3054
Geometric Standard Deviation (σ_g): 1.254
Pot Temperature (°C): 155
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 50
Particle Size Setting (volts): 75

Table I.6   Performance of Emersol 875 Isostearic Acid
in the Q127 Machine.

ΔNUMCON Δlr;g: >10-?;

DIAMETER (μm)
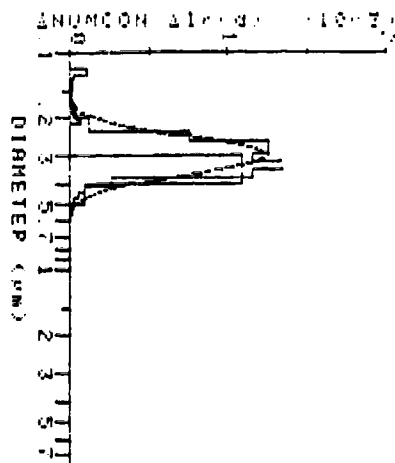
```
DATE 88/9/14   TIME 135500  PSLF
MAX CNTS/SEC=    618  SEC=    10
P:0-3 TPUN   0 BINS    1 00 ML/SEC
DILUTION RATIO       = 1 000E+000
TEMPERATURE     (C)= 2 200E+001
ATM PRESSURE (mm Hg)= 7 500E+002
REL HUMIDITY    (%)= 5 000E+001
A PARAMETER        = 0 000E+000
B PARAMETER        = 0 000E+000
C PARAMETER        = 0 000E+000
NUM CONC  (NUMB/cm3)= 2 241E+002
GEOM MEAN DIAM  (μm)= 2 995E-001
GEOM STANDARD DEV   = 1 219E+000
MASS CONC    (mg/m3)= 1 023E-002
UNDIL MASSCON(mg/m3)= 1 023E-002
MAX CNTS/SEC        = 6 184E+002
PEAK DIAMETER (μm)  = 3 347E-001
FIT NUM CONC (#/cm3)= 0 000E+000
FIT GEOM MN DIA (μm)= 1 000E-008
FIT GEOM STAND DEV  = 1 000E+002
FIT UNDIL M0 (mg/m3)= 0 000E+000
```

| PROBE RANGE=3 | TOT | CNTS= 616E |
BIN	DIA	COUNT	DISTN VALUE
0	.120	53	1.09E+002
1	.126	16	3.44E+001
2	.132	7	1.57E+001
3	.138	8	1.88E+001
4	.144	6	1.47E+001
5	.150	9	2.29E+001
6	.156	3	7.95E+000
7	.162	4	1.10E+001
8	.168	1	2.85E+000
9	.174	6	1.77E+001
10	.180	12	3.66E+001
11	.186	4	1.26E+001
12	.192	15	4.87E+001
13	.198	13	4.02E+001
14	.204	20	6.90E+001
	.210 (	5990=OVERCOUNT)	

| PROBE RANGE=2 | TOT | CNTS= 6134 |
BIN	DIA	COUNT	DISTN VALUE
0	.170	55	3.38E+001
1	.200	179	1.28E+002
2	.230	931	7.51E+002
3	.260	1376	1.26E+003
4	.290	1141	1.16E+003
5	.320	1212	1.35E+003
6	.350	950	1.16E+003
7	.380	200	2.63E+002
8	.410	73	1.03E+002
9	.440	40	6.06E+001
10	.470	16	2.59E+001
11	.500	1	1.72E+000
12	.530	11	2.00E+001
13	.560	4	7.66E+000
14	.590	2	4.03E+000
	.620 (	3=OVERCOUNT)	

| PROBE RANGE=1 | TOT | CNTS= 3377 |
BIN	DIA	COUNT	DISTN VALUE
0	.300	3153	1.10E+003
1	.400	203	9.10E+001
2	.500	19	1.04E+001
3	.600	2	1.30E+000
4	.700	0	0.00E+000
5	.800	0	0.00E+000
6	.900	0	0.00E+000
7	1.000	0	0.00E+000
8	1.100	0	0.00E+000
9	1.200	0	0.00E+000
10	1.300	0	0.00E+000
11	1.400	0	0.00E+000
12	1.500	0	0.00E+000
13	1.600	0	0.00E+000
14	1.700	0	0.00E+000
	1.800 (	0=OVERCOUNT)	

| PROBE RANGE=0 | TOT | CNTS= 0 |
BIN	DIA	COUNT	DISTN VALUE
0	1.500	0	0.00E+000
1	1.900	0	0.00E+000
2	2.300	0	0.00E+000
3	2.700	0	0.00E+000
4	3.100	0	0.00E+000
5	3.500	0	0.00E+000
6	3.900	0	0.00E+000
7	4.300	0	0.00E+000
8	4.700	0	0.00E+000
9	5.100	0	0.00E+000
10	5.500	0	0.00E+000
11	5.900	0	0.00E+000
12	6.300	0	0.00E+000
13	6.700	0	0.00E+000
14	7.100	0	0.00E+000
	7.500 (	0=OVERCOUNT)	

Machine: Q127
Geometric Mean Diameter (μm): 0.2995
Geometric Standard Deviation (σ_g): 1.219
Pot Temperature (°C): 155
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 50
Particle Size Setting (volts): 70

Table I.7   Performance of Emersol 871 Isostearic Acid
in the Q127 Machine.

LOGNORM DISTRIBUTION 1 0 1

5C
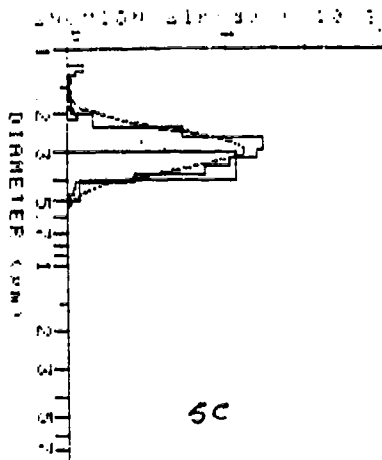
```
DATE 98/9.20    TIME 135910   PSLF
MAX CNTS/SEC=    574  SEC=    10
R:0-3 TRUN  0 BINS   1 00 ML/SEC
DILUTION RATIO       = 1.000E+000
TEMPERATURE     (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7 600E+002
REL HUMIDITY    (%)= 5.000E+001
A PARAMETER          = 0 000E+000
B PARAMETER          = 0 000E+000
C PARAMETER          = 0 000E+000
NUM CONC  (NUMB/cm3)= 5.838E+002
GEOM MEAN DIAM  (um)= 2.944E-001
GEOM STANDARD DEV    = 1 230E+000
MASS CONC    (mg/m3)= 9.191E-003
UNDIL MASSCON(mg/m3)= 9.191E-003
MAX CNTS/SEC         = 5 743E+002
PEAK DIAMETER (um)   = 2 746E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-006
FIT GEOM STAND DEV   = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

```
PROBE RANGE=3    TOT CNTS=   5619
BIN  DIA     COUNT  DISTN VALUE
 0   .120      53   1.09E+002
 1   .126      27   5.80E+001
 2   .132       8   1.80E+001
 3   .138      15   3 52E+001
 4   .144       6   1 47E+001
 5   .150       5   1 27E+001
 6   .156      13   3 44E+001
 7   .162       9   2.47E+001
 8   .168       7   1 99E+001
 9   .174      13   3.83E+001
10   .180       9   2.74E+001
11   .186       6   1 89E+001
12   .192      13   4.23E+001
13   .198      17   5 69E+001
14   .204      21   7 24E+001
     .210  <  5397=OVERCOUNT>
```

```
PROBE RANGE=3    TOT CNTS=    574
BIN  DIA     COUNT  DISTN VALUE
 0   .170      50   3 05E+001
 1   .200     228   1.63E+002
 2   .230     896   7.23E+002
 3   .260    1354   1.24E+003
 4   .290    1161   1.30E+003
 5   .320     921   1 03E+003
 6   .350     711   8 65E+002
 7   .380     320   4.21E+002
 8   .410      41   5 81E+001
 9   .440      14   2 15E+001
10   .470      10   1 62E+001
11   .500       3   5 15E+000
12   .530       1   1.82E+000
13   .560       1   1.92E+000
14   .590       2   4.03E+000
     .620  <     0=OVERCOUNT>
```

```
PROBE RANGE=1    TOT CNTS=   3255
BIN  DIA     COUNT  DISTN VALUE
 0   .300    3055   1.06E+003
 1   .400     188   6.43E+001
 2   .500       6   3 29E+000
 3   .600       3   1 95E+000
 4   .700       0   0.00E+000
 5   .800       0   0 00E+000
 6   .900       0   0 00E+000
 7  1.000       0   0 00E+000
 8  1.100       0   0 00E+000
 9  1.200       0   0.00E+000
10  1.300       0   0 00E+000
11  1.400       0   0 00E+000
12  1.500       0   0 00E+000
13  1.600       0   0.00E+000
14  1.700       0   0 00E+000
    1.800  <     0=OVERCOUNT>
```

```
PROBE RANGE=0    TOT CNTS=    0
BIN  DIA     COUNT  DISTN VALUE
 0  1.500       0   0.00E+000
 1  1.900       0   0.00E+000
 2  2.300       0   0.00E+000
 3  2.700       0   0.00E+000
 4  3.100       0   0.00E+000
 5  3.500       0   0.00E+000
 6  3.900       0   0.00E+000
 7  4.300       0   0.00E+000
 8  4.700       0   0.00E+000
 9  5.100       0   0.00E+000
10  5.500       0   0.00E+000
11  5.900       0   0.00E+000
12  6.300       0   0.00E+000
13  6.700       0   0.00E+000
14  7.100       0   0 00E+000
    7.500  <     0=OVERCOUNT>
```

Machine: Q127
Geometric Mean Diameter (μm): 0.2944
Geometric Standard Deviation (σ_g): 1.230
Pot Temperature (°C): 180
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 50
Particle Size Setting (volts): 75

Table I.8   Performance of Emery 3004 Synthetic Hydrocarbon in the Q127 Machine.

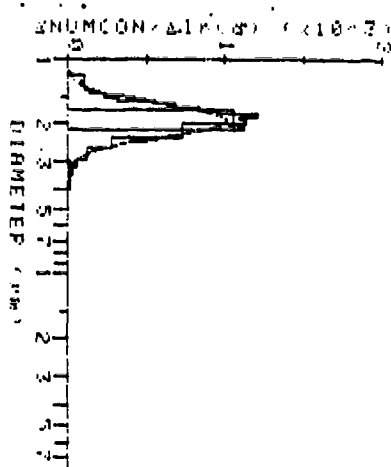| BIN	DIA	COUNT	DISTN VALUE
0	.170	1710	1.05E+003
1	.200	1014	7.26E+002
2	.230	348	2.84E+002
3	.260	133	1.22E+002
4	.290	55	5.59E+001
5	.320	24	2.68E+001
6	.350	1	1.22E+000
7	.380	1	1.32E+000
8	.410	0	0.00E+000
9	.440	0	0.00E+000
10	.470	0	0.00E+000
11	.500	0	0.00E+000
12	.530	0	0.00E+000
13	.560	0	0.00E+000
14	.590	0	0.00E+000
	.620 (		0=OVERCOUNT)

PROBE RANGE=1   TOT CNTS=   62

BIN	DIA	COUNT	DISTN VALUE
0	.300	62	2.16E+001
1	.400	0	0.00E+000
2	.500	0	0.00E+000
3	.600	0	0.00E+000
4	.700	0	0.00E+000
5	.800	0	0.00E+000
6	.900	0	0.00E+000
7	1.000	0	0.00E+000
8	1.100	0	0.00E+000
9	1.200	0	0.00E+000
10	1.300	0	0.00E+000
11	1.400	0	0.00E+000
12	1.500	0	0.00E+000
13	1.600	0	0.00E+000
14	1.700	0	0.00E+000
	1.800 (		0=OVERCOUNT)

PROBE RANGE=0   TOT CNTS=   0

BIN	DIA	COUNT	DISTN VALUE
0	1.500	0	0.00E+000
1	1.900	0	0.00E+000
2	2.300	0	0.00E+000
3	2.700	0	0.00E+000
4	3.100	0	0.00E+000
5	3.500	0	0.00E+000
6	3.900	0	0.00E+000
7	4.300	0	0.00E+000
8	4.700	0	0.00E+000
9	5.100	0	0.00E+000
10	5.500	0	0.00E+000
11	5.900	0	0.00E+000
12	6.300	0	0.00E+000
13	6.700	0	0.00E+000
14	7.100	0	0.00E+000
	7.500 (		0=OVERCOUNT)

```
DATE 88/9/21    TIME 140900   PSLF
MAX CNTS/SEC=    437   SEC=    10
P:0-3 TPUN   0 BINS    100 ML/SEC
DILUTION RATIO        = 1.000E+000
TEMPERATURE      (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY      (%)= 5.000E+001
A PARAMETER          = 0.000E+000
B PARAMETER          = 0.000E+000
C PARAMETER          = 0.000E+000
NUM CONC  (NUMB/cm3)= 4.439E+002
GEOM MEAN DIAM  (um)= 1.926E-001
GEOM STANDARD DEV   = 1.191E+000
MASS CONC   (mg/m3)= 1.918E-003
UNDIL MASSCON(mg/m3)= 1.918E-003
MAX CNTS/SEC         = 4.374E+002
PEAK DIAMETER  (um) = 1.830E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-008
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

PROBE RANGE=3   TOT CNTS=   4374

BIN	DIA	COUNT	DISTN VALUE
0	.120	51	1.05E+002
1	.126	41	8.01E+001
2	.132	51	1.15E+002
3	.138	56	1.32E+002
4	.144	93	2.20E+002
5	.150	129	3.26E+002
6	.156	207	5.48E+002
7	.162	250	6.87E+002
8	.168	291	8.29E+002
9	.174	328	9.68E+002
10	.180	395	1.20E+003
11	.186	345	1.09E+003
12	.192	350	1.14E+003
13	.198	307	1.03E+003
14	.204	323	1.11E+003
	.210 (		1158=OVERCOUNT)

Machine: Q127
Geometric Mean Diameter (µm): 0.1926
Geometric Standard Deviation (σ_g): 1.191
Pot Temperature (°C): 195
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 35
Particle Size Setting (volts): 87

Table I.9   Performance of Emery 3006 Synthetic Hydrocarbon in the Q127 Machine.

ΔNUMCON/(Δln·d) (10^3)

DIAMETER (μm)
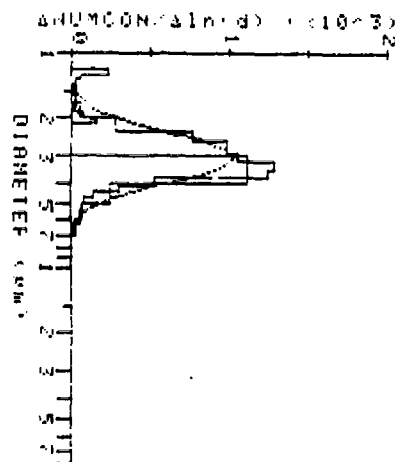
DATE 88/9/29   TIME 135020   PSLF
MAX CNTS/SEC=   669   SEC=   10
P:0-3 TRUN 0 BINS   1 00 ML/SEC
DILUTION RATIO   = 1.000E+000
TEMPERATURE   (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY   (%)= 5.000E+001
A PARAMETER   = 0.000E+000
B PARAMETER   = 0.000E+000
C PARAMETER   = 0.000E+000
NUM CONC   (NUMB/cm3)= 6.831E+002
GEOM MEAN DIAM (μm)= 3.052E-001
GEOM STANDARD DEV   = 1.305E+000
MASS CONC   (mg/m3)= 1.383E-002
UNDIL MASSCON(mg/m3)= 1.383E-002
MAX CNTS/SEC   = 6.688E+002
PEAK DIAMETER (μm) = 3.347E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (μm)= 1.000E-006
FIT GEOM STAND DEV = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000

PROBE RANGE=3   TOT CNTS=   6651
BIN   DIA   COUNT   DISTN VALUE
0   .120   118   2.42E+002
1   .126   29   6.23E+001
2   .132   15   3.37E+001
3   .139   14   3.29E+001
4   .144   11   2.69E+001
5   .150   7   1.78E+001
6   .156   11   2.91E+001
7   .162   11   3.02E+001
8   .168   11   3.13E+001
9   .174   10   2.95E+001
10   .180   7   2.13E+001
11   .186   15   4.72E+001
12   .192   22   7.15E+001
13   .198   35   1.21E+002
14   .204   48   1.66E+002
     .210 (6286=OVERCOUNT)

PROBE RANGE=2   TOT CNTS=   6588
BIN   DIA   COUNT   DISTN VALUE
1   .200   352   4.80E+002
2   .230   941   7.68E+002
3   .260   1087   9.92E+002
4   .290   1040   1.06E+003
5   .320   1156   1.29E+003
6   .350   1028   1.25E+003
7   .380   399   5.25E+002
8   .410   221   3.13E+002
9   .440   100   1.52E+002
10   .470   50   8.08E+001
11   .500   39   6.69E+001
12   .530   34   6.18E+001
13   .560   30   5.75E+001
14   .590   29   5.85E+001
     .620 (44=OVERCOUNT)

PROBE RANGE=1   TOT CNTS=   3976
BIN   DIA   COUNT   DISTN VALUE
0   .300   3210   1.12E+003
1   .400   567   2.54E+002
2   .500   128   7.02E+001
3   .600   56   3.63E+001
4   .700   12   8.99E+000
5   .800   5   4.25E+000
6   .900   0   0.00E+000
7   1.000   0   0.00E+000
8   1.100   0   0.00E+000
9   1.200   0   0.00E+000
10 1.300   0   0.00E+000
11 1.400   0   0.00E+000
12 1.500   0   0.00E+000
13 1.600   0   0.00E+000
14 1.700   0   0.00E+000
    1.800 (0=OVERCOUNT)

PROBE RANGE=0   TOT CNTS=   0
BIN   DIA   COUNT   DISTN VALUE
0   1.500   0   0.00E+000
1   1.900   0   0.00E+000
2   2.300   0   0.00E+000
3   2.700   0   0.00E+000
4   3.100   0   0.00E+000
5   3.500   0   0.00E+000
6   3.900   0   0.00E+000
7   4.300   0   0.00E+000
8   4.700   0   0.00E+000
9   5.100   0   0.00E+000
10 5.500   0   0.00E+000
11 5.900   0   0.00E+000
12 6.300   0   0.00E+000
13 6.700   0   0.00E+000
14 7.100   0   0.00E+000
    7.500 (0=OVERCOUNT)

Machine: Q127
Geometric Mean Diameter (μm): 0.3052
Geometric Standard Deviation (σ_g): 1.305
Pot Temperature (°C): 160
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 49
Particle Size Setting (volts): 75

Table I.10   Performance of Industrene 206LP Oleic Acid
in the Q127 Machine.

ENUMCON ...

DIAMETER (μm)

```
PROBE RANGE=2     TOT CNTS=   1600
BIN  DIA    COUNT   DISTN VALUE
  0  .170    770     4.74E+002
  1  .200    425     7.04E+002
  2  .230    190     1.55E+002
  3  .260    104     9.52E+001
  4  .290     47     4.77E+001
  5  .320     37     4.13E+001
  6  .350     16     1.95E+001
  7  .380      1     1.32E+000
  8  .410      3     4.25E+000
  9  .440      2     3.03E+000
 10  .470      0     0.00E+000
 11  .500      0     0.00E+000
 12  .530      0     0.00E+000
 13  .560      0     0.00E+000
 14  .590      0     0.00E+000
     .620 (      5=OVERCOUNT)
```

```
PROBE RANGE=1     TOT CNTS=    101
BIN  DIA    COUNT   DISTN VALUE
  0  .300     94     3.27E+001
  1  .400      2     8.96E-001
  2  .500      3     1.65E+000
  3  .600      2     1.30E+000
  4  .700      0     0.00E+000
  5  .800      0     0.00E+000
  6  .900      0     0.00E+000
  7 1.000      0     0.00E+000
  8 1.100      0     0.00E+000
  9 1.200      0     0.00E+000
 10 1.300      0     0.00E+000
 11 1.400      0     0.00E+000
 12 1.500      0     0.00E+000
 13 1.600      0     0.00E+000
 14 1.700      0     0.00E+000
    1.800 (      0=OVERCOUNT)
```

```
PROBE RANGE=0     TOT CNTS=      0
BIN  DIA    COUNT   DISTN VALUE
  0 1.500      0     0.00E+000
  1 1.900      0     0.00E+000
  2 2.300      0     0.00E+000
  3 2.700      0     0.00E+000
  4 3.100      0     0.00E+000
  5 3.500      0     0.00E+000
  6 3.900      0     0.00E+000
  7 4.300      0     0.00E+000
  8 4.700      0     0.00E+000
  9 5.100      0     0.00E+000
 10 5.500      0     0.00E+000
 11 5.900      0     0.00E+000
 12 6.300      0     0.00E+000
 13 6.700      0     0.00E+000
 14 7.100      0     0.00E+000
    7.500 (      0=OVERCOUNT)
```

```
DATE 88/9/29    TIME 185730   PSLF
MAX CNTS/SEC=    249   SEC=     10
R:0-3 TRUN  0 BINS   1.00 ML/SEC
DILUTION RATIO          = 1.000E+000
TEMPERATURE      (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY     (%)= 5.000E+001
A PARAMETER         = 0.000E+000
B PARAMETER         = 0.000E+000
C PARAMETER         = 0.000E+000
NUM CONC   (NUMB/cm3)= 1.539E+001
GEOM MEAN DIAM   (um)= 1.874E-001
GEOM STANDARD DEV    = 1.253E+000
MASS CONC    (mg/m3)= 1.151E-003
UNDIL MASSCON(mg/m3)= 1.151E-003
MAX CNTS/SEC        = 2.491E+002
PEAK DIAMETER   (um)= 1.830E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (um)= 1.000E-008
FIT GEOM STAND DEV  = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000
```

```
PROBE RANGE=3     TOT CNTS=   2491
BIN  DIA    COUNT   DISTN VALUE
  0  .120     54     1.11E+002
  1  .126     62     1.33E+002
  2  .132     61     1.37E+002
  3  .138     78     1.83E+002
  4  .144    123     3.01E+002
  5  .150    147     3.75E+002
  6  .156    149     3.92E+002
  7  .162    167     4.59E+002
  8  .168    165     4.70E+002
  9  .174    176     5.19E+002
 10  .180    173     5.28E+002
 11  .186    133     4.35E+002
 12  .192    138     4.48E+002
 13  .198    106     3.55E+002
 14  .204    125     4.31E+002
     .210 (    530=OVERCOUNT)
```

Machine: Q127
Geometric Mean Diameter (μm): 0.1874
Geometric Standard Deviation (σ_g): 1.253
Pot Temperature (°C): 160
Quench Air Flow Rate (lpm): 90
Vapor Flow Rate (lpm): 10
Owl Setting (degrees): 35
Particle Size Setting (volts): 72

Table I.11   Performance of Emersol 233LL Oleic Acid
in the Q127 Machine.
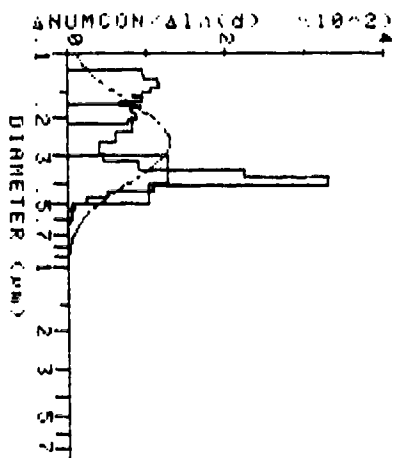
DATE 88/7/7   TIME 151017   PSLF
MAX CNTS/SEC=   136   SEC=   17
R:0-3 TRUN 0 BINS   1.00 ML/SEC
DILUTION RATIO   = 1.000E+000
TEMPERATURE   (C)= 2.200E+001
ATM PRESSURE (mm Hg)= 7.600E+002
REL HUMIDITY   (%)= 5.000E+001
A PARAMETER   = 0.000E+000
B PARAMETER   = 0.000E+000
C PARAMETER   = 0.000E+000
NUM CONC (NUMB/cm3)= 1.400E+002
GEOM MEAN DIAM (µm)= 2.581E-001
GEOM STANDARD DEV   = 1.542E+000
MASS CONC   (mg/m3)= 2.457E-003
UNDIL MASSCON(mg/m3)= 2.457E-003
MAX CNTS/SEC   = 1.361E+002
PEAK DIAMETER (µm) = 3.947E-001
FIT NUM CONC (#/cm3)= 0.000E+000
FIT GEOM MN DIA (µm)= 1.000E-008
FIT GEOM STAND DEV = 1.000E+002
FIT UNDIL M0 (mg/m3)= 0.000E+000

PROBE RANGE=3   TOT CNTS=   2314

BIN	DIA	COUNT	DISTN VALUE
0	.120	79	9.52E+001
1	.126	78	9.86E+001
2	.132	86	1.14E+002
3	.138	85	1.17E+002
4	.144	73	1.05E+002
5	.150	63	9.45E+001
6	.156	52	8.10E+001
7	.162	59	9.54E+001
8	.168	40	6.71E+001
9	.174	53	9.26E+001
10	.180	44	7.89E+001
11	.186	44	8.15E+001
12	.192	46	8.79E+001
13	.198	44	9.67E+001
14	.204	38	7.71E+001
	.210 (	1430=OVERCOUNT)	

PROBE RANGE=2   TOT CNTS=   .???

BIN	DIA	COUNT	DISTN VALUE
0	.170	227	8.22E+001
1	.200	197	8.29E+001
2	.230	126	6.05E+001
3	.260	74	3.99E+001
4	.290	76	4.54E+001
5	.320	137	8.99E+001
6	.350	311	2.22E+002
7	.380	423	3.27E+002
8	.410	131	1.09E+002
9	.440	57	5.08E+001
10	.470	26	2.47E+001
11	.500	10	1.01E+001
12	.530	2	2.14E+000
13	.560	0	0.00E+000
14	.590	3	3.56E+000
	.620 (	0=OVERCOUNT)	

PROBE RANGE=1   TOT CNTS=   1048

BIN	DIA	COUNT	DISTN VALUE
0	.300	622	1.27E+002
1	.400	396	1.04E+002
2	.500	23	7.42E+000
3	.600	5	1.91E+000
4	.700	2	8.81E-001
5	.800	0	0.00E+000
6	.900	0	0.00E+000
7	1.000	0	0.00E+000
8	1.100	0	0.00E+000
9	1.200	0	0.00E+000
10	1.300	0	0.00E+000
11	1.400	0	0.00E+000
12	1.500	0	0.00E+000
13	1.600	0	0.00E+000
14	1.700	0	0.00E+000
	1.800 (	0=OVERCOUNT)	

PROBE RANGE=0   TOT CNTS=   0

BIN	DIA	COUNT	DISTN VALUE
0	1.500	0	0.00E+000
1	1.900	0	0.00E+000
2	2.300	0	0.00E+000
3	2.700	0	0.00E+000
4	3.100	0	0.00E+000
5	3.500	0	0.00E+000
6	3.900	0	0.00E+000
7	4.300	0	0.00E+000
8	4.700	0	0.00E+000
9	5.100	0	0.00E+000
10	5.500	0	0.00E+000
11	5.900	0	0.00E+000
12	6.300	0	0.00E+000
13	6.700	0	0.00E+000
14	7.100	0	0.00E+000
	7.500 (	0=OVERCOUNT)	

Machine: Q127
Geometric Mean Diameter (µm): 0.2581
Geometric Standard Deviation (σ_g): 1.542
Pot Temperature (°C): 172
Quench Air Flow Rate (lpm): 80
Vapor Flow Rate (lpm): 20
Owl Setting (degrees): 48
Particle Size Setting (volts): 100

Table I.12   Performance of DOP in the Q127 Machine.

```
PROBE RANGE=2    TOT CNTS=
BIN   DIA    COUNT   DISTN VALUE
 0    .170     66     4.71E+000
 1    .200     97     5.17E+000
 2    .230   1047     1.00E+002
 3    .260   3500     3.77E+002
 4    .290   4069     4.95E+002
 5    .320   2954     3.88E+002
 6    .350   1468     2.10E+002
 7    .380    185     2.38E+001
 8    .410     47     5.16E+000
 9    .440     13     2.72E+000
10    .470      4     7.51E-001
11    .500      3     4.04E-001
12    .530      1     2.14E-001
13    .560      0     0.00E+000
14    .590      0     0.00E+000
      .620  (      0=OVERCOUNT)
```

```
PROBE RANGE=1    TOT CNTS=    8507
BIN   DIA    COUNT   DISTN VALUE
 0    .300   8429     3.45E+003
 1    .400     74     5.90E+000
 2    .500      2     1.29E-001
 3    .600      2     1.53E-001
 4    .700      0     0.00E+000
 5    .800      0     0.00E+000
 6    .900      0     0.00E+000
 7   1.000      0     0.00E+000
 8   1.100      0     0.00E+000
 9   1.200      0     0.00E+000
10   1.300      0     0.00E+000
11   1.400      0     0.00E+000
12   1.500      0     0.00E+000
13   1.600      0     0.00E+000
14   1.700      0     0.00E+000
     1.800  (      0=OVERCOUNT)
```

```
PROBE RANGE=0    TOT CNTS=        0
BIN   DIA    COUNT   DISTN VALUE
 0   1.500      0     0.00E+000
 1   1.900      0     0.00E+000
 2   2.300      0     0.00E+000
 3   2.700      0     0.00E+000
 4   3.100      0     0.00E+000
 5   3.500      0     0.00E+000
 6   3.900      0     0.00E+000
 7   4.300      0     0.00E+000
 8   4.700      0     0.00E+000
 9   5.100      0     0.00E+000
10   5.500      0     0.00E+000
11   5.900      0     0.00E+000
12   6.300      0     0.00E+000
13   6.700      0     0.00E+000
14   7.100      0     0.00E+000
     7.500  (      0=OVERCOUNT)
```

```
DATE 88 9 7      TIME :71611   PSLF
MAX CNTS/SEC=     151  S0.=     17
P 0-3 TPUN  0 BINS   5.00 ML/SEC
DILUTION RATIO      =  1.000E+000
TEMPERATURE     (C)=  2.200E+001
ATM PRESSURE (mm Hg)=  7.600E+002
REL HUMIDITY    (%)=  5.000E+001
A PARAMETER         =  0.000E+000
B PARAMETER         =  0.000E+000
C PARAMETER         =  0.000E+000
NUM CONC  (NUM/cm3)=  1.590E+002
GEOM MEAN DIAM  (um)=  3.017E-001
GEOM STANDARD DEV   =  1.161E+000
MASS CONC   (mg/m3)=  2.490E-003
UNOIL MASSCON(mg/m3)=  2.490E-003
MAX CNTS/SEC        =  7.914E+002
PEAK DIAMETER (um)  =  3.046E-001
FIT NUM CONC (#/cm3)=  0.000E+000
FIT GEOM MN DIA (um)=  1.000E-008
FIT GEOM STAND DEV  =  1.000E+002
FIT UNOIL MC (mg/m3)=  0.000E+000
```

```
PROBE RANGE=3    TOT CNTS=   13453
BIN   DIA    COUNT   DISTN VALUE
 0    .120     59     1.42E+001
 1    .126     31     7.84E+000
 2    .132      9     2.38E+000
 3    .138      7     1.94E+000
 4    .144      4     1.15E+000
 5    .150      7     2.10E+000
 6    .156      4     1.25E+000
 7    .162      5     1.62E+000
 8    .168      6     2.01E+000
 9    .174      6     2.08E+000
10    .180      5     1.79E+000
11    .186      4     1.65E+000
12    .192      9     3.44E+000
13    .198      7     2.76E+000
14    .204     11     4.06E+000
      .210  (    737=OVERCOUNT)
```

Machine: Q127
Geometric Mean Diameter (μm): 0.3017
Geometric Standard Deviation (σ_g): 1.161
Pot Temperature (°C): 185
Quench Air Flow Rate (lpm): 82
Vapor Flow Rate (lpm): 18
Owl Setting (degrees): 38
Particle Size Setting (volts): 65

Table I.13   Performance of DOS in the Q127 Machine.

APPENDIX J

CALIBRATION, LIMITATIONS AND OTHER PERTINENT
ASPECTS OF THE PMS LASER AEROSOL SPECTROMETER,
MODEL LAS-X

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APPENDIX J

CALIBRATION, LIMITATIONS AND OTHER PERTINENT

ASPECTS OF THE PMS LASER AEROSOL SPECTROMETER,

MODEL LAS-X

by

Bernard V. Gerber, Consultant
Optimetrics, Inc.
2008 Hogback Road, Suite 6
Ann Arbor, Michigan

1.   BACKGROUND

The Laser Aerosol Spectrometer, Model LAS-X, made by Particle Measuring Systems, Inc. (PMS), 1855 South 57th Court, Boulder, Colorado 80301, is the key instrument in the program discussed in this report; it is also described briefly in Appendix E.

The objective of the present program was to find non-hazardous substitutes for di (2-ethylhexyl) phthalate (DEHP, also commonly called DOP) in test instrumentation generating aerosols by spray or thermal means (evaporation/condensation). The inclusion of two such systems was specified for this investigation; namely, the Q127 military standard DOP machine and the Los Alamos Monodispersed Aerosol Prototype Penetrometer (LAMAPP, Appendix E).

The PMS LAS-X laser aerosol spectrometer is an integral part of the LAMAPP system described in Appendix E, and is used to measure particle size distributions generated by that system. The generated size distributions are expected to fit a log-normal distribution characterized by two parameters; namely, a count median diameter (CMD) and a geometric standard deviation (σ_g).

For the present effort the desired goal was specified as a CMD of 0.3 μm diameter and a σ_g ("sigma g") of less than 1.2. It must be noted that these values are subject to change in the future. The Q127 has been in use without major alteration since World War II at which time, based on existant theory, it was thought that a 0.3 μm particle diameter (unit density) would be most effective in filter penetration.

The then-current aerosol technology was the basis for the design of the Q127 in its three essential components; i.e., generation, particle size measurement, and penetration measurement. Of particular relevance to this discussion is the particle size measurement technique.

The Q127 employs an electromechanical version of the "Owl"[J1], (a code name used in World War II), which measures the ratio of the intensities of the plane-polarized mutually-perpendicular components of white scattered light observed 90° to the incident beam. The measurement is accomplished through an analog; namely, the angle at which a rotatable polarizer balances the intensities in both halves of a fixed bipartite polarizer.

If the aerosol is nearly monodisperse, and is between 0.1 and 0.4 μm in diameter, then this angle is uniquely correlated to the particle size. It is known today, however, that the Owl will give non-unique readings for a polydisperse aerosol.

Hinds, et al,[J2] applied the laser aerosol spectrometer to the Q127 and compared the results to the Owl settings. They concluded that there were an infinite number of CMD-σ_g pairings that would give the same Owl reading. In particular, the Owl responded to an average particle size based on eighth power weighting.

Gerber[J3] identified a simple relationship based only on CMD and σ_g to calculate this. Hinds, et al,[J2] claimed the phenomenon would be significant for σ_g greater than 1.09. It has never been shown in the present investigation or in any other known study that the Q127 is capable of generating such a monodisperse aerosol.

Apparently, monodisperse generation has been assumed in the past but never validated even though laborious means (higher-order Tyndall spectra[J4], the gravitational battery[J5,J6]) were available to make this determination. The laser aerosol spectrometer now appears to be a rapid and relatively convenient means to measure CMD and possibly σ_g of the particle size distribution generated by the Q127 with some degree of accuracy and in relatively real time (with the aid of an integrated computer to quickly reduce the data).

However, the basis for such claims must be justified and it is the purpose of the following paragraphs to provide pertinent information, data, references, and comments. It must be noted that the present investigation used an early model LAS-X, but the essential features remain the same for current models. Some improvement in resolution can be expected by the use of current models, however.

2.   LAS-X DESCRIPTION

A schematic of the LAS-X optical system is shown in Figure J1, and the airflow diagram is shown in Figure J2. The laser is a hybrid He:Ne 632.8 nm tube (TEM$_{oo}$ mode). The active laser cavity provides an energy density in excess of 500 watts per square centimeter with a beam width of 300-1000 μm.

The aerosol sample, aspirated by a diaphragm pump, is aerodynamically focussed by a nozzle and surrounded by a clean air sheath in an attempt to position the particle stream (which is about 100 μm wide) at the focal point of a 5-mm parabolic mirror. The scattered laser light is collected over a solid angle greater than 2π steradians by the parabolic mirror.
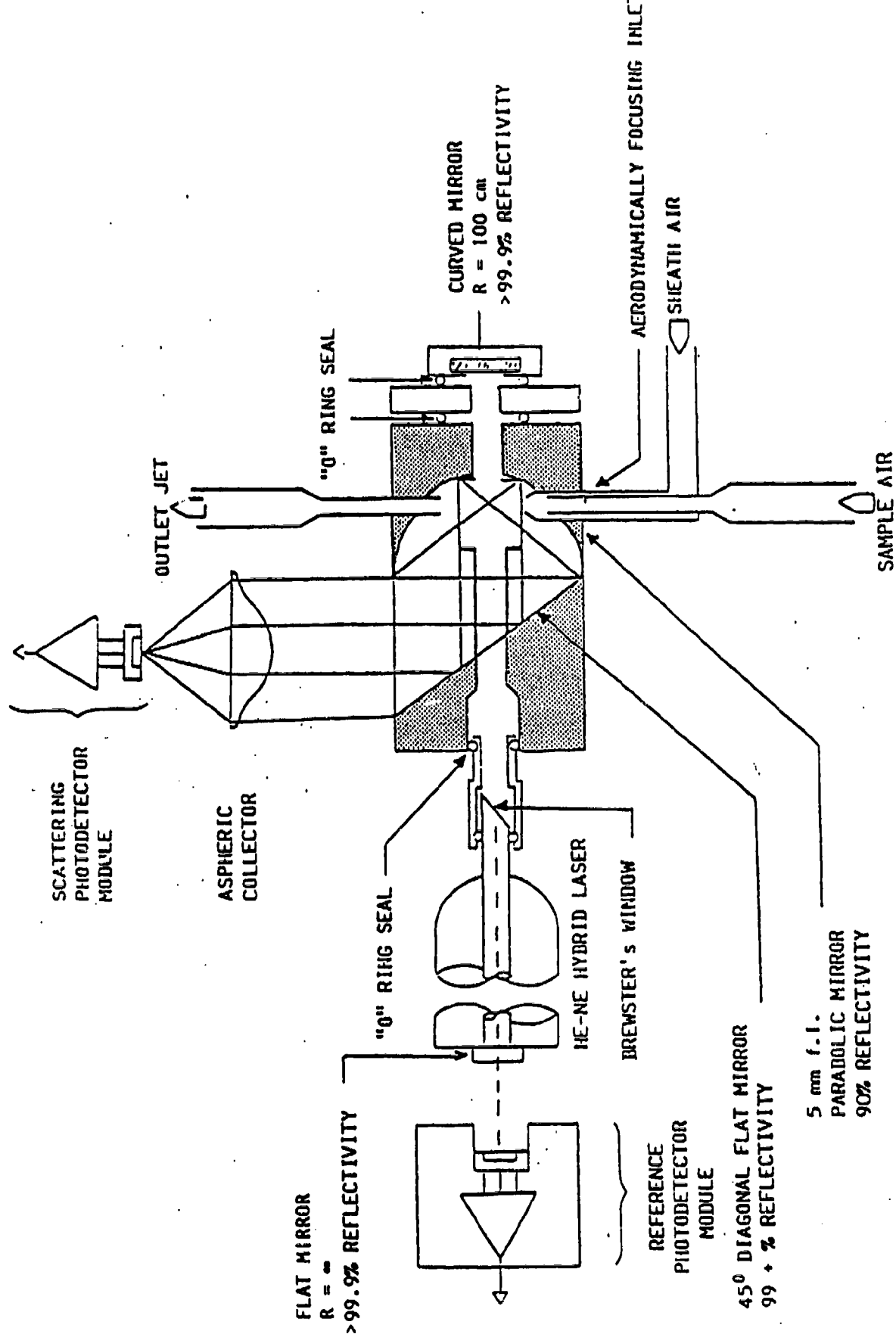
Figure J.1   LAS-X Optical System Diagram.
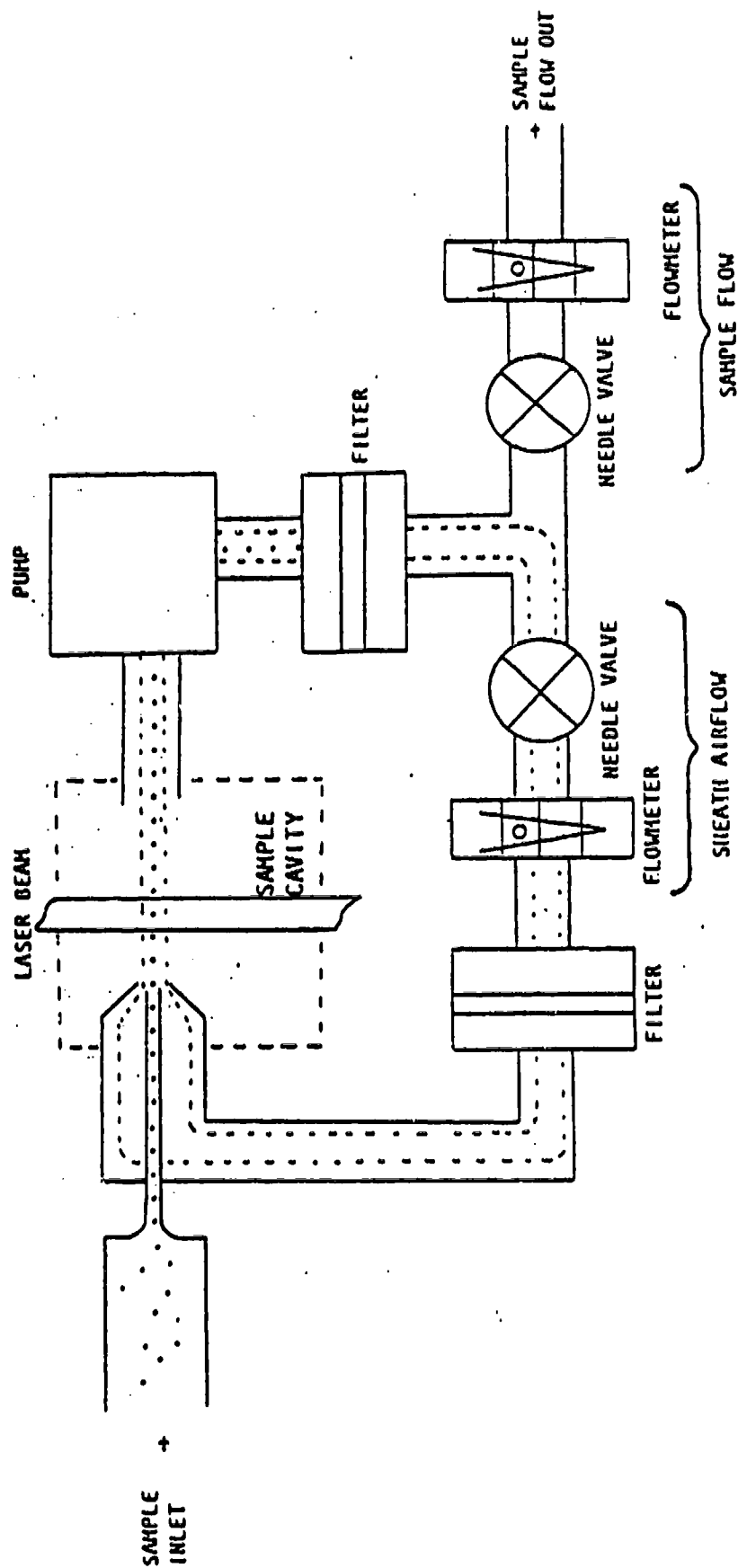
Figure J.2   LAS-X Airflow Diagram.

The collected light is reflected from a 45° diagonal flat mirror and is subsequently refocussed by an aspheric lens and presented to a photodiode detector. The signal pulses are processed by an integral pulse height analyzer whose reference voltage is derived from the illumination source (reference photodetector in Figure J1). Automatic gain control and programmable amplifiers provide size ranging and the large dynamic range of the instrument.

The instrument as used in these investigations is an older model that has four ranges covering 0.12-7.5 μm with each range divided into 15 size channels ("bins"), and one oversize channel. Each bin can count up to 20 million. All size classes are simultaneously sampled in the selected range, thus forming the basis for calling the instrument a "spectrometer".

Size ranges may be singly selected or, by choosing the "AUTO" mode, the instrument will sequence through all size ranges. Size range and size channel information is outputted along with the count data. Various output modes are available, including an RS232C serial port (8 ASCII decimal characters plus a space per word, 18 words per frame, line feed/18 words) for input to a computer.

This study used the HP85 component of the LAMAPP system; sample strip chart outputs are shown in Appendix I. Other integral output modes are a 7-column thermal printer, a 6-digit decimal display, and a 4-inch CRT histogram display (Appendix I). The sample flow and the sheath air flow can be varied by metering valves and monitored by in-line flowmeters.

Too high a particle concentration in the sample will cause "coincidence error" (multiple particles being counted as one). The smoke concentration from the Q127 is between three and four orders of magnitude too high for the present investigations. Therefore, two diluters (manufactured by Thermo-Systems, Inc., St. Paul, MN) were used in series to bring the aerosol concentrations within the LAS-X range of accuracy.

If required, additional information concerning the current LAS-X model and other models is readily available from PMS, address as above.

3. MEASUREMENT AND CALIBRATION OVERVIEW

The CMD range of interest in this investigation was 0.2-0.3 μm diameter. Polystyrene latex (PSL) particles with the appropriate characteristics are available and are used as calibration standards. These characteristics are: (1) availability in various discrete mean sizes; (2) extremely small standard deviation associated with the particle size distribution.

Recently, one particle distribution in the desired size range has been prepared by emulsion polymerization on a Space Shuttle mission, to maximize sphericity by minimizing gravity. It is available from the U.S. National Bureau of Standards (NBS 1691 SRM).

There are materiel and procedural factors in PSL calibration which are best discussed later in this appendix. The primary points which are to be discussed first deal with the basic validity of PSL as a calibration standard for LAS-X, and its use in current investigations.

PMS precalibrates the LAS-X at the factory before delivery. Garvey and Pinnick[J7] describe the calibration procedure in some detail. PSL results are used to determine a normalization constant to relate measured voltage to theoretical response (scattering cross-section per particle). The theoretical response from Mie theory is derived for spherical particles of known refractive index. PSL refractive index is between 1.58 and 1.59 (real index, non-complex), depending upon exact composition.[J8]

In general, the inherent LAS-X instrumental standard deviation is considerably larger than that of the PSL lattices (Knollenberg[J9]). Even if it is assumed that the aerodynamic sample stream focussing operation has been accomplished precisely, there remains the question of the uniformity of illumination.

The laser beam typically is about 800 μm in diameter[J10] at the point of intersection with the sample stream, which is about 100 μm in diameter. The laser beam intensity varies radially as a Gaussian distribution. R. Luehr, a PMS representative, has claimed that particle location variation typically could cause a plus or minus one bin PSL peak deviation.[J11] More will be said on this later, since it impacts directly on the capabilities of the LAS-X to measure the σ_g of a sample (although not so much the CMD measurement).

4.   CALIBRATION AND CMD MEASUREMENT: LAS-X

4.1   PSL Certification/Validation.

A particular PSL size choice should show maximum counts in only one channel, if chosen judiciously so as not to occur at the junction of two adjacent channels. Absolute calibration requires absolute standards and, in the size range of interest here, only the NBS standard meets that qualification.

The absolute sizes of the other materials has been a debatable point for many years. Various investigators[J12-J16] have remeasured selected PSL standards and checked the average particle size and standard deviation. The most current work[J16] is considered the most reliable.[J9] Table J.1. has been extracted from the report of Yamada, et al.[J16]

With one exception, the latest work indicates that nominal sizes are overestimates varying between the rough limits of one and 20 percent. One nominal size is underestimated by approximately 7%. The discrepancies in the particle size average are a source of great concern to those interested in absolute calibration. The discrepancies in σ_g are not of concern. Knollenberg[J9] (PMS) has done very recent work with a high-sensitivity laser aerosol spectrometer (HS-LAS) having 32 channels between 0.065 and 1.000 μm. The class widths vary from 0.005 to 0.100 μm over the specified range. He used two lasers of differing wavelength to extend the Rayleigh scattering region.

Table J.1   Nominal (Labelled) vs. Remeasured Values.

Average Diameter, Nominal (μm)	Average Diameter, Remeasured (μm)	Diameter Percent Difference (%)	σ, Nominal, (μm)	σ, Measured, (μm)	σ Percent Difference (%)
0.085	0.069	− 18.8	0.0055	0.0072	30.9
0.091	0.083	− 8.8	0.0058	0.0068	17.2
0.109	0.105	− 3.7	0.0027	0.0024	− 11.1
0.109	0.107	− 1.8	0.0027	0.0020	− 25.9
0.176	0.167	− 5.1	0.0023	0.0023	0.0
0.176	0.174	− 1.1	0.0023	0.0022	− 4.3
0.210	0.209	− 0.5	0.0100	0.0026	− 74.0
0.312	0.333	+ 6.7	0.0022	0.0048	118.0
0.330	0.327	− 0.9	0.0040	0.0024	− 40.0

The NBS standard was used as an absolute reference to adjust, by proportion, all results. The NBS standard has a certified size of 0.269 plus or minus 0.007 μm with a standard deviation of less than 0.0053 μm.

Table J.2. is extracted from the Knollenberg paper.[J9] Where the same samples were measured, excellent agreement with electron microscope measurements of Yamada is evident. It is concluded that sufficient information on PSL mean sizes in the range of interest exists to determine an accurate normalization constant[J7] which will calibrate (size vs channel) the LAS-X (for PSL refractive index = 1.586). The factory calibration is acceptable for submicron PSL particles.

4.2   Refractive Index Effects.

The theoretical light scattering response for spherical particles is a function of refractive index as well as particle size but, fortunately for the particle size range of present interest and for the refractive indices of the candidate substitute materials under consideration, the correction factor appears to be small. We may establish the size range of interest by considering the "two sigma" range (σ_g = 1.2) about the desired CMD.

This translates to (0.3/(2 x 1.2)) to (0.3 x (2 x 1.2)) or 0.12 − 0.72 μm diameter (0.06-0.36 μm radius). As previously stated, the refractive index for PSL is taken by PMS to be 1.586. The refractive index for DEHP is 1.485. The refractive index for water is 1.33. The candidate liquids can be expected to fall in the range 1.3 to 1.6.

Garvey and Pinnick[J7] have studied the response to particles of various refractive index of a PMS active scattering spectrometer probe (ASASP-X) which has essentially the same optics as the LAS-X.

Table J.2   Comparison of HS-LAS Measured Latex Particle Sizes
With Nominal Values.

Nominal Mean Diameter (μm)	Material	Standard Deviation (μm)	HS-LAS Ratioed Size
0.065	PSL	0.0069	0.063
0.085	PSL	0.0055	0.067
0.087	S/B	0.0046	0.089
0.091	PSL	0.0058	0.085
0.102	CML	0.0072	0.104
0.106	PSL	0.0053	0.103
0.109	PSL	0.0023	0.102
0.110	PSL	0.0047	0.104
0.123	PSL	0.0049	0.120
0.144	PSL	0.0037	0.136
0.173	PSL	0.0068	0.161
0.176	PSL	0.0023	0.162
0.198	PSL	0.0036	0.180
0.203	CML	0.0043	0.199
0.204	PSL	0.0020	0.190
0.215	PSL	0.0026	0.181
0.220	PSL	0.0065	0.220
0.261	PSL	0.0031	0.245
0.267	PSL	0.0033	0.269
0.269	PSL	nil	0.269
0.305	PSL	0.0084	0.300
0.320	PSL	0.0150	0.305
0.312	PSL	0.0020	0.320
0.364	S/B	0.0024	0.363
0.369	VT/TBS	0.0024	0.359
0.399	PVT	0.0060	0.374
0.412	PSL		0.392
0.460	PSL	0.0048	0.462

Material Code:

PSL	Polystyrene Latex
CML	Carboxylate Modified Latex
S/B	Styrene/Butadiene Copolymer
PVT	Polyvinyl Toluene
VT/TBS	Vinyl Toluene/Tertiary-Butyl Styrene

Figure J.3 is extracted from Reference J7 and forms the basis for the following comments. Calculations for DEHP yield a theoretical curve that falls between the 1.33 and 1.544 index curves. It is difficult to obtain numerical correction factors from Figure J.3. without access to the base numerical data.
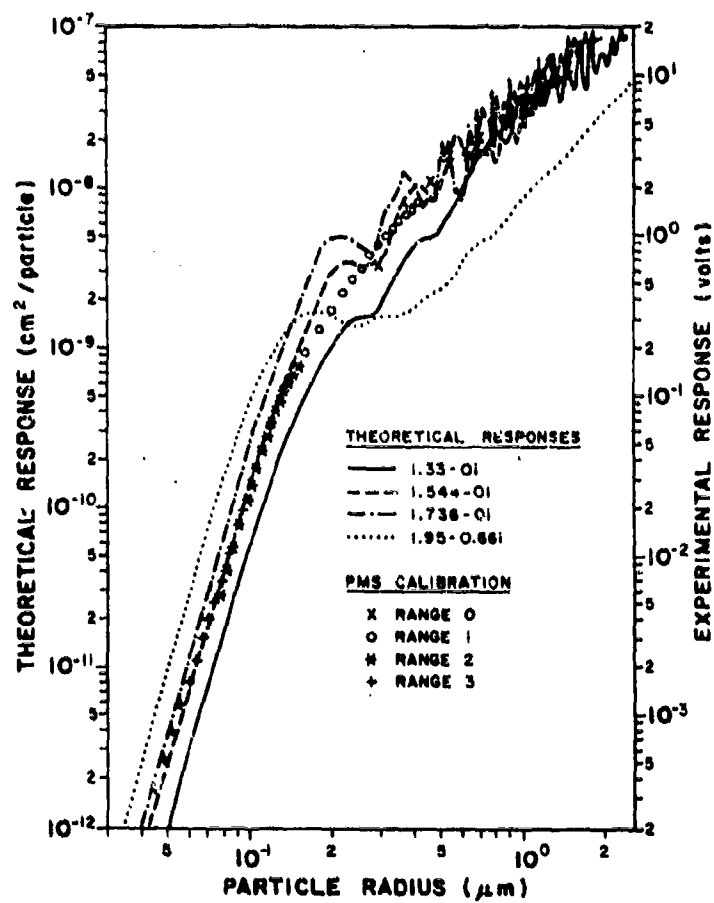
Figure J.3   Comparison of Theoretical ASASP-X Response Curves.

Garvey and Pinnick[J7] claim that water droplets (index = 1.33) are undersized by approximately 33% for particle diameters between 0.6 and 1.6 μm. This would be in the upper region of our interest, but we might expect DEHP to be undersized by about 70% of that value in the same range, or about 20-25%. Below a diameter of about 0.4 μm the undersizing is proportionally less. Our rough estimate is 10-15%. It is also evident that the sodium chloride curve (index = 1.544) and the PSL calibration points coincide within experimental capabilities.

The manufacturer of LAS-X (PMS) provides no information of this kind. It is concluded that the refractive index factor must be considered if one wishes to make extremely rigorous measurements of mean size on non-absorbing, spherical aerosols of materials other than PSL. This factor could be important in making claims as to the measured CMD but is much less important in the measurement of σ_g which is inherently a ratio so that absolute errors will tend to cancel.

5.   "SIGMA G" (σ_g) MEASUREMENT/ LAS-X

5.1   **Available Data.**

Published data on the measurement of σ_g of sample aerosols are not extensive. Salzman, et al,[J17] report measuring a σ_g of 1.33 and 1.2 for 0.312 and 0.176 μm PSL particles, respectively. (These particular sizes are Dow nominal measurements which have since been remeasured). Hinds, et al,[J4] published a large scale readable histogram for 0.234 μm nominal PSL measured with an active scattering aerosol spectrometer probe (PMS model ASASP-300). (Porstendorfer[J15] reports 0.206 μm for these PSL particles on remeasurement). This author calculates an estimated σ_g of 1.16 from that histogram.

Yamada, et al,[J18] have published the most recent and comprehensive paper to date comparing LAS-X measurements with their own electron microscopy results.[J16] Table J.3 is an extract of pertinent data from that paper. In stream alignment tests they were able to measure σ_g values as low as 1.04 with the LAS-X. It is to be noted that the LAS-X values are in every case higher than the electron microscopy values, as expected.

CRDEC requested that PMS provide data on factory PSL measurements using the LAS-X in the range 0.2 to 0.3 μm diameter. Mr. Robert Luehr, PMS, supplied the information shown in Tables J.4 through J.7, which follow.

The data in Tables J.4-J.7 were obtained using a current LAS-X system with better resolution than the older model used in our investigation. This current model has the capability of covering the span 0.09 to 3.00 μm in four ranges. These data were analyzed by the present author, and a few observations can be made immediately.

First, note that, where appropriate, the nominal and the Knollenberg size (see Table J.2) is given. Second, note that the data in Table J.5 undoubtedly are for the NBS certified standard (0.269 plus or minus 0.007 μm). Third, note that the LAS-X measurement of this standard seems to be displaced by one channel. Fourth, note that Tables J.4-J.6 truncate at smaller particle sizes; this is most severe in Table J.6.

Table J.3   PSL Measured by LAS-X and Electron Microscopy (EM).

Nominal Diameter (μm)	Mean Diameter by EM, (μm)	σ_g, by EM	σ_g, by LAS-X
0.109	0.105	1.04	1.10
0.176	0.167	1.03	1.08
0.210	0.209	1.03	1.08
0.312	0.333	1.02	1.09
0.330	0.327	1.02	1.13

Table J.4   LAS-X Sizing and Standard Deviation Accuracy.

Range 1, Channel	Raw Count	Size Range (μm)	Interval
15	0	0.71-0.75	0.04
14	1	0.67-0.71	0.04
13	1	0.63-0.67	0.04
12	0	0.59-0.63	0.04
11	0	0.55-0.59	0.04
10	1	0.51-0.55	0.04
9	1	0.47-0.51	0.04
8	3	0.43-0.47	0.04
7	10	0.39-0.43	0.04
6	39	0.35-0.39	0.04
5	54	0.32-0.35	0.03
4	281	0.29-0.32	0.03
3	4118	0.26-0.29	0.03
2	1030	0.23-0.26	0.03
1	359	0.20-0.23	0.03

Source: Robert Luehr (10 June 1988).

Particle Size = 0.305 μm (Mfr. size)
              0.300 μm (PMS size)

It is a well known statistical fact that such truncation will cause an underestimation of sigma g. Schemes have been devised to improve such estimates.[19] Numerical[20] and tabular[21] procedures for these schemes have been published. Finally, note that there are many low level counts in the small particle bins of Range 2 in Table J.7. It is likely that these are due to spurious surfactant counts or to the use of water containing impurities in making up the diluted PSL suspensions. Cleanliness will clearly affect resulting sigma g values.

Table J.5   LAS-X Sizing and Standard Deviation Accuracy.

Range 1, Channel	Raw Count	Size Range (μm)	Interval
15	0	0.71-0.75	0.04
14	0	0.67-0.71	0.04
13	0	0.63-0.67	0.04
12	0	0.59-0.63	0.04
11	0	0.55-0.59	0.04
10	0	0.51-0.55	0.04
9	0	0.47-0.51	0.04
8	1	0.43-0.47	0.04
7	0	0.39-0.43	0.04
6	4	0.35-0.39	0.04
5	3	0.32-0.35	0.03
4	1	0.29-0.32	0.03
3	28	0.26-0.29	0.03
2	261	0.23-0.26	0.03
1	67	0.20-0.23	0.03

Source: Robert Luehr (10 June 1988).

Particle Size = 0.269 μm

Table J.6   LAS-X Sizing and Standard Deviation Accuracy.

Range 1, Channel	Raw Count	Size Range (μm)	Interval
15	0	0.71-0.75	0.04
14	0	0.67-0.71	0.04
13	0	0.63-0.67	0.04
12	0	0.59-0.63	0.04
11	0	0.55-0.59	0.04
10	1	0.51-0.55	0.04
9	0	0.47-0.51	0.04
8	3	0.43-0.47	0.04
7	18	0.39-0.43	0.04
6	98	0.35-0.39	0.04
5	95	0.32-0.35	0.03
4	139	0.29-0.32	0.03
3	131	0.26-0.29	0.03
2	592	0.23-0.26	0.03
1	493	0.20-0.23	0.03

Source: Robert Luehr (10 June 1988).

Particle Size = 0.261 μm (Mfr. size)
              0.245 μm (PMS size)

Table J.7 LAS-X Sizing and Standard Deviation Accuracy.

Channel	Range	Raw Count	Size Range (μm)	Interval
15	1	0	0.71-0.75	0.04
14	1	0	0.67-0.71	0.04
13	1	1	0.63-0.67	0.04
12	1	0	0.59-0.63	0.04
11	1	0	0.55-0.59	0.04
10	1	0	0.51-0.55	0.04
9	1	0	0.47-0.51	0.04
8	1	2	0.43-0.47	0.04
7	1	10	0.39-0.43	0.04
6	1	14	0.35-0.39	0.04
5	1	30	0.32-0.35	0.03
4	1	37	0.29-0.32	0.03
3	1	78	0.26-0.29	0.03
2	1	107	0.23-0.26	0.03
1	1	608	0.20-0.23	0.03
15	2	290	0.193-0.20	0.007
14	2	153	0.186-0.193	0.007
13	2	76	0.179-0.186	0.007
12	2	38	0.172-0.179	0.007
11	2	35	0.165-0.172	0.007
10	2	29	0.158-0.165	0.007
9	2	21	0.151-0.158	0.007
8	2	32	0.144-0.151	0.007
7	2	26	0.137-0.144	0.007
6	2	28	0.130-0.137	0.007
5	2	25	0.124-0.130	0.006
4	2	22	0.118-0.124	0.006
3	2	20	0.112-0.118	0.006
2	2	49	0.106-0.112	0.006
1	2	87	0.100-0.106	0.006

Source: Robert Luehr (10 June 1988).

Particle Size = 0.220 μm

These circumstances are not unlike those which have been encountered by CRDEC investigators. We can conclude that PMS procedures are not significantly superior to those now employed at CRDEC, but the question remains to be resolved whether they can be improved.

Although one can compute mean size statistics (CMD and average diameter) from the data in Tables J.4 -J.7 , our focus is only on sigma g (σ_g). Table J.8. gives the calculated results.

Table J.8   Sigma-g (σ_g) From PMS Data for Selected PSL Measurements Using the LAS-X Aerosol Spectrometer.

Nominal Diameter (μm)	PMS Diameter (μm)	σ_g
0.305	0.300	1.09
0.269	0.269	1.09
0.261	0.245	1.19
0.220	0.220	1.31

Unfortunately, there is only general but not exact correspondence between the nominal diameters measured here and those measured by Yamada (Table J.3.). However we can see that in two of four cases the PMS operator obtained low sigma g values, but in the other two cases the results were much higher.

One result, i.e., σ_g = 1.19, is in the numerical region often obtained by CRDEC as well. The other, σ_g = 1.31, is substantially higher. Therefore, it is concluded that control has not been established over the factors that govern the PSL calibration procedure to the extent necessary to have confidence in LAS-X-based estimates of sigma g.

5.2   Implied LAS-X Performance Limits.

The very best performance reported to date has been that of Yamada, et al,[J18] who reported a sigma g of 1.04 for LAS-X and 1.03 for electron microscopy. The LAS-X variance includes the PSL distribution variance and statistically it is known that the variance of the convolution of two normal distributions is the sum of the variances of the members.

The square of in sigma g is the variance involved here. The LAS-X measured variance is the convolution result, the PSL variance is one of the component members, and the square root of the LAS-X inherent variance is the sought-after result. The best data from Yamada, et al,[J18] imply that the LAS-X inherent sigma g is better than 1.04 and that it can measure sigma g = 1.04 for 0.210 μm PSL.

The best value achieved by PMS was sigma g = 1.09, which was a typical Yamada value as well. Yamada, et al,[J15] show that the PSL sigma g is about 1.02 to 1.03 in the size ranges for which PMS achieved 1.09. To be conservative 1.02 was used and the result was an inherent LAS-X sigma g estimate of 1.087.

Since the Dow PSL batches for which sigma g estimates are available are few in number, it is well to note that a fairly good estimate can be obtained from a formula involving only mean size and sigma, both of which usually are available. The formula is:

$$\text{"sigma g" } (\sigma_{g}) = \frac{\text{sigma}}{\text{mean size}} + 1 \qquad\qquad (J.1\ )$$

This formula is based on several assumptions and should only be applied to nearly monodisperse particle distributions.

Garvey and Pinnick[J7] state that plus or minus 2 to 3 channels is typical distribution broadening for PSL measurements. Channel width is, of course, physically a signal voltage difference which is factory-adjusted but is transformed to an interval in units of micrometers.

The available data on PSL electron microscopy (including original Dow data) all indicate a sigma such that PSL measurement should fall into only one LAS-X channel. The more accurate remeasurements of original Dow data do not change that observation. It does not appear unreasonable to estimate the LAS-X performance sigma in terms of channel width.

The basis for this is the statistical fact that plus or minus one sigma around the mean represents about 64% of a normal distributior, while plus or minus two sigma encloses about 95% and plus or minus three sigma encloses nearly 100%.

The data in Tables J.4 and J.5 represent the best that PMS was able to do in measuring sigma g. A half width of 4-5 channels appears to enclose almost all of the distribution. Considering this to be three sigma we estimate sigma to lie between 1.33 and 1.66 channels or, on average, 1.5 channels. Formula (J.1) can be invoked for each channel to transform sigma g estimates.

Note that the estimate will vary with particle size since the channel interval remains constant over the range. If tne resolution is constant, it will be a greater percentage for smaller particles and thus will affect sigma g estimates. Table J.9 for the CRDEC LAS-X model type bears this out.

This analysis yields the additional insight that LAS-X measurements centered on the high side of a range will have a better resolution of sigma g than measurements made on the low side. It is noted that Tables J.4 , J.5 and J.6 are centered on the low end of the range, implying that the machine could do better. Table J.7 shows a range change in the middle, and ideally should have the experiments shown repeated with improved procedures before conclusions can be drawn.

Nevertheless, <u>it appears that the estimation procedure just</u> <u>outlined is an acceptable way to represent the empirical database and</u> place expectations on LAS-X performance in measuring sigma g (σ_{g}).

As stated previously however, the best performances have not been achieved consistently and the factors controlling consistent performance have not been defined. These factors include both LAS-X set-up and PSL calibration procedures. These are discussed in the following sections of this appendix.

Table J.9   Estimated Sigma-g (σ_g) Resolution for the LAS-X
(0.12 to 7.5 μm Model).

Channel	Range	Size Range (μm)	σ_g Resolution
1	0	1.5-1.9	1.24
8	0	4.3-4.7	1.09
15	0	7.1-7.5	1.06
1	1	0.3-0.4	1.29
8	1	1.00-1.10	1.10
15	1	1.70-1.80	1.06
1	2	0.17-0.20	1.16
8	2	0.38-0.41	1.08
15	2	0.59-0.62	1.05
1	3	0.120-0.126	1.07
8	3	0.162-0.168	1.06
15	3	0.204-0.210	1.04

6.   SET-UPS/ MATERIALS/ PROCEDURES

6.1   LAS-X.

Yamada, et al,[J18] performed comprehensive tests on the effects of LAS-X set-up on PSL calibration. The set-up controls of relevance are: (1) stream alignment; (2) sample airflow rate; (3) sheath air flow rate.

By far the most critical factor is stream alignment. The aerodynamic focussing is done with an adjustable nozzle and it is extremely critical that the vertical alignment screw be correctly set. A rotation of only 1/8 to 1/4 turn of the screw, according to Yamada, et al.,[J18] can shift the CMD and sigma g drastically.

For example, a 1/4 turn misalignment caused distribution broadening and sigma g increased from 1.04 to 1.15. Garvey and Pinnick[J7] refer to this criticality as well. The Japanese investigators frequently realigned the nozzle.

It is concluded that this realignment should be performed anytime a change is noted using a reliable PSL standard. The change includes the channel position of the peak and the channel halfwidth.

For example, the data in Table J.5 would have called for realignment since the peak is "off". This procedure must be made routine.

PMS recommends that PSL validations be done at very low streamflow rates but Yamada, et al,[J18] found only small decreases in CMD and increases in sigma g between 0.5 and 2.0 cm^3 of flow per second. Similar results were found for sheath airflow variations between 10 and 40 cubic centimeters per second. Yamada, et al,[J18] conclude that PMS recommendations for set-up of these adjustments is acceptable.

6.2   Aerosol Dilution.

The LAS-X can incur coincidence errors at high particle concentrations. The aerosol output of PSL nebulizers must be diluted accurately and reproducibly if quantitative number concentration results for the sample stream are required. The LAMAPP has a built-in capillary diluter for PSL. CRDEC employed two capillary diluters (made by TSI and described elsewhere) in series with the output of the DOP machine.

Yamada, et al,[J18] inserted the PSL nebulizer output into a large duct in which filtered air was flowing. A LAS-X sample was extracted downstream. The flow rate in the duct ratioed to the extracted LAS-X sample flow rate gives the dilution ratio. Hinds, et al,[J4] used a similar dilution system. Yamada, et al,[J18] made all measurements in a concentration range between 100 and 1000 particles per cm^3. Coincidence is almost negligible in this range.

It is easier to track the particle concentration in terms of particles per second since the LAS-X directly measures count per channel and the elapsed time in seconds for that range measurement. The transformation of particles per cubic centimeter to particles per second merely involves multiplying the former by the flow rate in cubic centimeters per second. Since Yamada, et al,[J18] used a flow rate of 1 cm^3/sec, the values of 100-1000 still apply.

These values are quite conservative since PMS claims[J22] 90% counting accuracy at 17,000 counts per second. In the judgement of this author, investigators should work below 1000 counts per second for calibration/validation measurements, and could work at counts as high as 5000-8000 per second for practical sample assessments.

6.3   Electrostatic Neutralization.

Garvey and Pinnick[J7] and Yamada, et al,[J18] all used a radioactive charge neutralizer for PSL work since nebulization yields charged particles. The electrostatic factor requires further investigation and may be related to the consistently superior results achieved by the Japanese investigators.

6.4   PSL Standards.

PSL suspensions contain emulsifying agents (surfactants) in solution which will be carried along with the PSL particles into the nebulized droplets. On drying, these agents should form small particles that can confuse PSL measurements.

Yamada, et al,[J18] ignored the first channel counts in the smallest size range in their PSL calculations. The LAMAPP manual recommends ignoring the first six channels. The data in Table J.7. indicate many particles in most channels. <u>This author concludes that this aspect is still an uncontrolled area worthy of further investigation</u>.

CRDEC results on surfactant-free PSL available from Polysciences, Inc.,[J23] show a vast improvement in small channel "noise". Bangs[J8] discusses methods of removing surfactant from PSL suspensions. This could possibly be done without changing the mean size or sigma.

6.5 <u>Clean Water and PSL Dilution</u>,

<u>The need for clean water in making up PSL suspension dilutions cannot be overemphasized</u>. At the very least one should use singly-distilled water, but preferably triply-distilled water. The use of ultra-filters should be investigated.

6.6 <u>PSL Dilution Ratio</u>.

PSL suspensions are sprayed using a nebulizer and the resulting droplet aerosol is dried to form the PSL aerosol. However, note that in order to achieve the PSL size seen under an electron microscope, each nebulized droplet should contain no more than one PSL particle. In order for this to occur the majority of nebulized droplets will contain no particles at all.

Of course, it should be noted that no process of this sort can be perfect but can only asymptotically approach perfection after a certain practical level has been achieved. In the present case, there will always be some probability that a particle doublet or larger aggregate will be found among the singlets.

Raabe[J24] has analyzed this problem mathematically and numerically. The following empirical relationship was developed which is of great value in PMS calibration work:

$$y = \frac{F (MMD)^3 e^{4.5 \ln^2 \sigma_g} \cdot (1-(e^{\ln^2 \sigma_g})/2)}{(1 - R) D^3} \qquad (J.2.)$$

where:
- y = the dilution ratio required;
- F = fraction by volume of particles in the stock PSL suspension;
- MMD = mass median diameter of the particle size distribution generated by the nebulizer;
- σ_g = geometric standard deviation of the particle size distribution generated by the nebulizer;
- R = single ratio desired;
- D = diameter of the monodisperse spheres.

Equation (J.2.) was found to hold for values of R greater than 0.9 and sigma g (σ_g) less than 2.1. Estimations of the MMD and sigma g for the DeVilbiss and other nebulizers are tabulated by Corn and Esmen.[J25]

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For example, MMD = 4 μm, σ_g = 1.8, F = 0.10, R = 0.95 and D = 0.35 μm is a representative case. From Equation (J.2.), one calculates a dilution ratio of 6.6×10^4; i.e., one part stock suspension in 66,000 parts water. Probably any convenient ratio between 10^4 and 10^5 would be adequate in view of the gross estimates of MMD and sigma g employed.

6.7   Overview.

In summary, it is clear that all procedural and set-up requirements must be adhered to rigorously.

7.   CONCLUSIONS

●   It is concluded that sufficient information on PSL mean sizes in the range of interest exists to determine an accurate normalization constant which will calibrate the LAS-X (for PSL refractive index = 1.586). The factory calibration is acceptable for submicron PSL particles.

●   It is concluded that the refractive index factor must be considered if one wishes to make extremely rigorous measurements of mean size on non-absorbing, spherical sample aerosols other than PSL.

●   It is concluded that control has not been established over the factors which govern the PSL calibration procedure, to the extent necessary to have confidence in LAS-X-based estimates of sigma g (σ_g).

●   It is concluded that the LAS-X stream injection nozzle should be realigned anytime a change is noted in the peak channel position or number of channels bounding the distribution for any reliable PSL standard.

●   It is concluded that all LAS-X and PSL set-up and procedural requirements must be adhered to rigorously.

8.   RECOMMENDATIONS

●   It is recommended that the most current sensitive model of the LAS-X be employed in any investigation proposing to measure the sigma g (σ_g) of aerosol distributions.

●   It is recommended that NBS PSL standards be used as primary standards to validate LAS-X performance.

●   It is recommended that PSL transfer standards which are surfactant-free be made from existing stocks, and then remeasured by electron microscopy.

●   It is recommended that investigations be carried out to determine the factors that govern the accuracy, precision and consistency of sigma g (σ_g) measurements using the LAS-X.

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